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Separation of niobium and tantalum in liquid extraction

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SEPARATION OF NIOBIUM AND TANTALUM BY LIQUID EXTRACTION

by

Ernest Lee Koerner, Jr.

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SUMMARY

Niobium, also known as columbium, is one of the new industrial metals likely to play an important role in industrial processing in the near future. Its high melting point (4376° F.) and low cross section for neutron absorption (1.1 barns) makes it of special interest to the Atomic Energy Commission. Since tantalum, which invariably accompanies niobium in its ores, has a somewhat higher cross section for neutron absorption (21 barns) there is considerable interest in developing an industrial process for producing tantalum-free niobium. Tantalum itself is a valuable metal because of its high melting point (5160° F.) and its resistance to most corrosive chemicals.

The purpose of this research was to find an economical method of producing a niobium oxide product containing as little tantalum and other impurities as possible starting with a typical niobium-rich ore or concentrate. The process selected as a result of the research consisted of the following processing steps:

1. Digestion of the ore or concentrate with hydrofluoric acid.
2. Extraction of niobium and tantalum from the digested mass with an organic solvent such as methyl isobutyl ketone.
3. Separation of tantalum and niobium by continuous countercurrent multistage extraction using an organic solvent and an aqueous scrubbing solvent.

4. Separation of niobium from other impurities by a second solvent extraction step using an organic solvent.
5. Stripping of the niobium and tantalum from their solvents and regeneration of solvents.

The process as outlined above was studied on a small scale and demonstrated on a somewhat larger scale so that a more accurate cost estimate could be made. Several pounds of niobium oxide containing less than 700 parts per million of tantalum oxide were produced. Several pounds of tantalum oxide containing less than 100 parts per million of niobium oxide were produced. Both purity values were the limit of detection for the spectrographic methods employed.

Preliminary cost estimates were made for production of purified niobium and tantalum oxides from an ore concentrate assaying 63 per cent niobium oxide and 7 per cent tantalum oxide. The basis chosen was a plant producing 300,000 pounds of total oxides per year or 270,000 pounds niobium oxide and 30,000 pounds tantalum oxide. Estimated chemical and total operating costs for one pound of either tantalum or niobium oxide were $1.89 and $2.80.

INTRODUCTION

Niobium and tantalum have had an interesting history. In 1801 Hatchett discovered niobium in a Connecticut mineral. Since niobium-bearing minerals without tantalum are virtually unknown, the first investigators were dealing with mixtures of these two chemically similar elements. The presence of titanium in some cases caused additional complications. Before their final identification, seven names had been ascribed to new elements that were thought to be present in these minerals. Marignac finally identified the two elements in 1866 by separating them as complex potassium fluorides by fractional crystallization. He found that the complex niobium fluoride was isomorphous with the known salts $K_2TiF_6 \cdot H_2O$ and $K_2WO_2F_4 \cdot H_2O$, which indicated that the valence of niobium was +5 and the formula of the salt was $K_2NbOF_5 \cdot H_2O$.

The first industrial importance of niobium resulted from its property of combining with carbon in steel to form stable niobium carbide. It is used as an addition agent to 18-8 chrome-nickel types of stainless steel to prevent intergranular corrosion. More recently, niobium has been mentioned as a possible structural material in nuclear reactors because of its corrosion resistance, high-temperature strength, and low neutron absorption. Because of the high neutron absorption of tantalum, any niobium used within a reactor would necessarily be required to be low in tantalum contamination.

Other possible uses of niobium are for gas turbine blade alloys and high-velocity, rapid-fire machine gun barrels. The former application would allow gas turbines to operate at higher temperatures than those now in use. Present gun liners do not have a satisfactory life. Work on molybdenum liners has not resulted in a production model. If costs are not prohibitive, the high melting points of niobium and tantalum and their alloys make them logical candidates for trial.

The physical property which makes niobium interesting for these and other applications is a melting point of 4376° F. This is roughly 1600-1700° F. higher than iron, cobalt, or nickel, which are the base metals for alloys useful to 1650° F. In addition, this is only 370° F. lower than the melting point of molybdenum, which is the base for alloys useful to at least 2000° F. (if protected from oxidation). In contrast to molybdenum, the oxide of niobium is relatively non-volatile and, therefore, may be easier to protect by alloying or coating.

For all of the above applications, niobium and tantalum must compete with relatively low cost metals. Future demand, therefore, will increase only if the price makes it competitive.

Presently the Fansteel Metallurgical Corporation is the sole producer of niobium metal. The present consumption of columbite-tantalite ores does not exceed 10,000 tons per year with only a small fraction being converted to niobium metal. During World War II, the world reserves were estimated as equivalent to 15,000,000 pounds of contained niobium and tantalum.

Present known reserves are of the order of ten times this figure in columbites and one hundred times including pyrochlore minerals.

The price of tantalum metal varies from 65 to 125 dollars a pound; niobium from 230 to 300 dollars a pound. The high cost is attributed partly to the fractional crystallization process presently used to separate the niobium and tantalum. Another factor which raises the cost is the fusion method of opening the ore.

It was the object of this investigation to propose, develop, and test a process for recovering niobium and tantalum oxides from their ores. The process selected as a result of this study is shown schematically in Figure 1. The columbite-tantalite ore was dissolved in 70 per cent hydrofluoric acid. Methyl isobutyl ketone (hexone) was used to extract the niobium and tantalum fluorides away from the gangue materials of the ore. This hexone solution of niobium and tantalum fluorides was used as feed material for the extraction separation. The fluoride salts were best suited to separation by solvent extraction since chlorides, nitrates, and sulfates exist only in dilute solutions.

The extraction apparatus shown in Figure 1 performed the actual separation of niobium and tantalum. The hexone preferentially extracted the tantalum, leaving tantalum-free niobium in the aqueous phase. A second extractor then extracted the niobium into another hexone phase separating it from the impurities in the aqueous phase. It was found that nine extraction stages would produce an extract of tantalum containing less than 100 parts per million of niobium and a raffinate of niobium containing

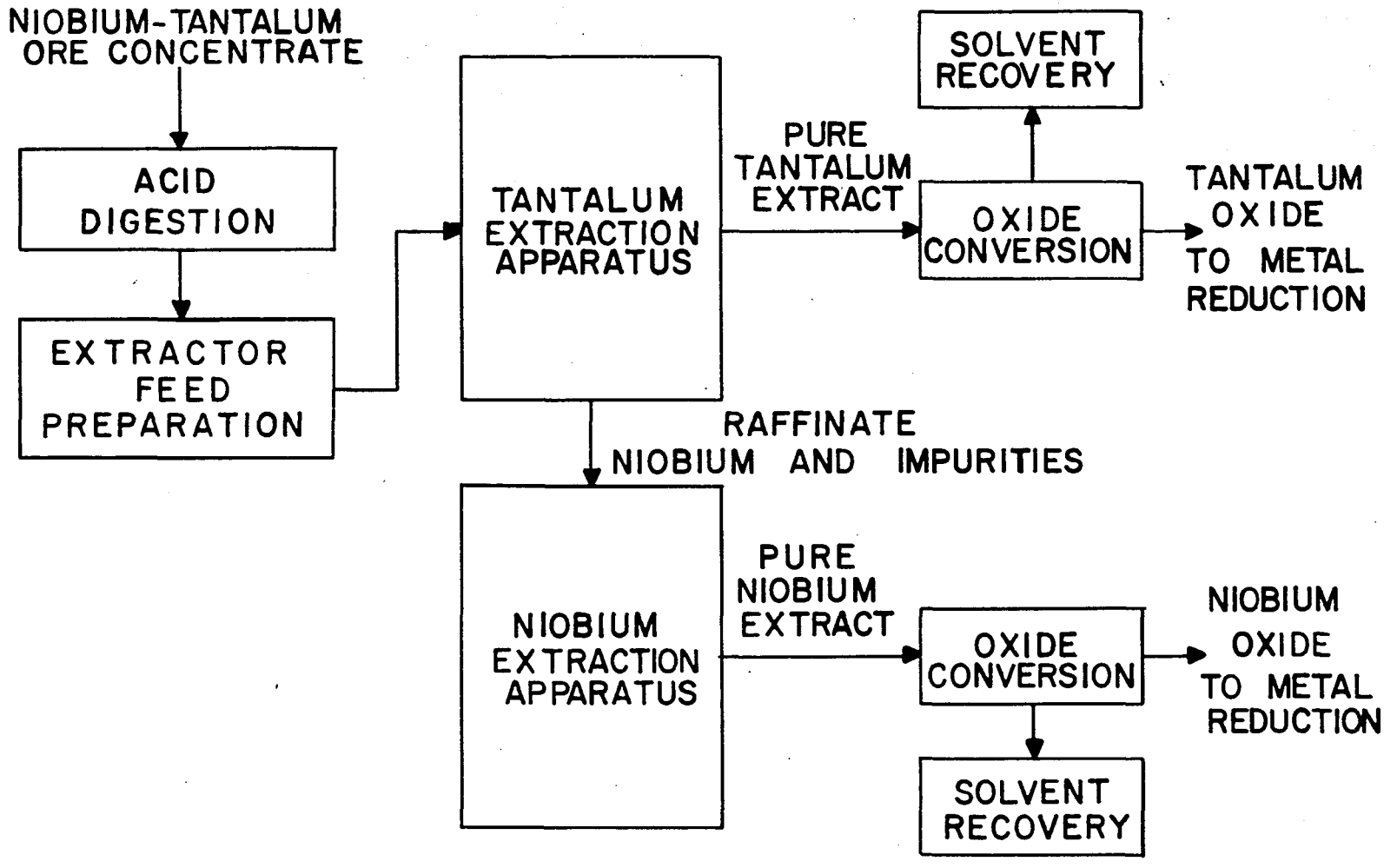

Figure 1. Proposed process for the separation of niobium and tantalum

less than 700 parts per million of tantalum. The purified tantalum and niobium fractions were removed from the hexone solvents by filtration after precipitation of the hydroxides with ammonia. The solvent streams were recovered, regenerated by mixing with sulfuric acid, and recycled. The purified hydroxides were calcined to tantalum and niobium oxides.

The simulated column technique was employed to obtain equilibrium extraction data. This procedure involved a series of batch contacts operated in such a manner as to approach steady state in a countercurrent extraction operation. The use of the procedure was successful in predicting product composition in continuous extraction runs.

Most of the investigation was concerned with the opening of the ore, the purification of the extractor feed solution, and the actual separation. Attempts to strip the solvents by various aqueous solutions were not successful so that resort was made to direct precipitation of the tantalum and niobium fluorides in the organic phase. The final product form of the tantalum and niobium were the oxides. These oxides were assumed suitable for metal reduction but if other salts proved more useful, they could be obtained by a simple modification in the process or by direct conversion of the oxides. Based upon methods developed in laboratory and pilot plant studies, a cost estimate of chemical and operating charges was compiled.

PREVIOUS WORK

The most important source of tantalum and niobium is a ferrous columbate-tantalate, $Fe(Nb\text{-}TaO_3)_2$. When niobium predominates, the mineral is called columbite, and when the tantalum predominates, tantalite. Manganese is sometimes found in place of iron. Columbite and tantalite are heavy minerals, the specific gravity varying from 5.3 to 7.3 with increasing tantalum content. They are usually associated with pegmatite dikes. The most important niobium-bearing minerals are listed in Table 1 (1).

During World War II, the world reserves were estimated as equivalent to 15,000,000 pounds of contained niobium and tantalum. Present known reserves are of the order of ten times this figure in columbites and one hundred times including pyrochlores. Pyrochlore is a mineral of the type $NaCaNb_2O_6F$, but K, Mg, Fe, Si, Sn, Ta, Ce, V, U, Th, and P may also be present.

Columbite ore is essentially all foreign, Nigeria being the most important source. However, large quantities of lower grade ores are known to exist on the North American continent. Table 2 describes most of the known deposits of niobium (2).

The present commercial method for the opening of columbite-tantalite ores involves a basic fusion with molten caustic at 650° C. In this process the pulverized ore is fused with caustic soda which converts the tantalum and niobium content of the mineral partly into the form of sodium

Table 1. Niobium-bearing minerals[a]

Name	Composition	Per cent		Specific gravity	Moh's hardness
		Nb_2O_5	Ta_2O_5		
Series:					
Columbite (theory)	$FeNb_2O_6$	78.72	—		
Tantalite (theory)	$FeTa_2O_6$	—	86.01		
Columbite	$(Fe,Mn)(Nb,Ta)_2O_6$	26–78	1–48	5.1–6.8	6
Tantalite	$(Fe,Mn)(Ta,Nb)_2O_6$	2–40	42–84	6–7.8	6–6.5
Series:					
Manganocolumbite	$(Mn,Fe)(Nb,Ta)_2O_6$	30–75	5–40	5.2–6.4	6
Manganotantalite	$(Mn,Fe)(Ta,Nb)_2O_6$	4–35	35–82	6–7.8	6–6.5
Stibiocolumbite–stibiotantalite series	$(Sb,Bi)(Nb,Ta)O_4$	1–48	1–60	5.5–7.5	6–7.3
Pyrochlore	$NaCaNb_2O_6F$	30–64	1–33	4.2–4.4	5–5.5
Yttrotantalite	$(Fe,Y,U,Ca)(Nb,Ta,Zn,Sn)O_4$	1–20	37–56	5.5–6.8	5–5.5
Fergusonite	$(Y,Er,Ce,Fe)(Nb,Ta,Ti)O_4$	14–46	4–43	5.6–5.8	5.5–6.5
Samarskite	$(Y,Er,Ce,U,Fe,Th)(Nb,Ta,Ti)_2O_6$	27–47	2–27	5.6–5.8	5–6
Euchynite	$(Ce,Ca,Fe,Th)(Ti,Nb)_2O_6$	23–37	?–7	4.9–5.1	5–6
Series:					
Euxenite	$(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$	15–41	1–6	4.7–5	5.5–6.5
Polycrase	$(Y,Ca,Ce,U,Th)(Ti,Nb,Ta)_2O_6$	4–20	?–14	4.7–5.9	5.5–6.5

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Table 2. Location and estimated reserves of niobium deposits

Location	Ore tonnage	Per cent Nb_2O_5	Tons Nb_2O_5	Remarks
			COLUMBITE	
Nigeria	-	-	57,000 proved 13,000 indicated	Partly by-product from tin operations
Idaho	-	-	8,000	Also contains euxenite, samarskite, and fergusonite
			PYROCHLORE	
Africa				
Tanganyika	10,000,000	0.3	30,000	Probably reserves much larger
Kenya	30,000,000	0.7	210,000	Also contains 3.1 per cent rare earth oxides
Uganda	200,000,000	0.3	600,000	Also contains 0.8 per cent zircon and 14 per cent P_2O_5
No. Rhodesia	-	-	-	Pyrochlore prospect
Uganda	-	-	-	Pyrochlore prospect
Nigeria	140,000,000	0.26	364,000	Pyrochlore in unweathered granite
Brazil	Possibly very large	2.0	-	Pyrochlore, euxenite and samarskite
Canada				
Newman Island	5-10,000,000	0.5	25-50,000	Underground mining beneath lake
Nemegos, Ontario	32,000,000	0.246	78,700	Reserves probably can be enlarged, koppite, pyrochlore and perovskite
Oka, Quebec	10,000,000 present 100,000,000 ultimate	0.2-0.3 -	200-300,000 -	Pyrochlore and perovskite. Open pit mining

tantalate and niobate, and partly into iron tantalate and niobate. Unlike the mineral itself, iron tantalate and niobate are readily decomposed by mineral acids. Sodium tantalate and niobate are practically insoluble in water containing free alkali, so that, when the fusion mass is treated with water, a large portion of the free alkali is removed by decantation. The mixed iron and sodium tantalates and niobates are finally removed from the fusion extract by filtration and are digested with hot hydrochloric acid which leaves a fairly white mixture of the earth acids. This precipitate is thoroughly washed with water to remove all iron and other soluble impurities (3).

Several investigators have reviewed the various methods for separating niobium and tantalum salts up to about 1945 (4, 5, 6). The process developed by Marignac (7) in 1866, with some variations, is the only method used commercially. In this process niobic and tantalic acids are dissolved in a minimum amount of hydrofluoric acid. The solution is saturated with potassium fluoride, evaporated and cooled. The tantalum is removed as potassium fluotantalate crystals, K_2TaF_7. After further evaporating and cooling, the niobium is removed as potassium pentafluoniobate crystals, $K_2NbOF_5 \cdot H_2O$. This separation is based on the difference in solubility in water of the two double potassium salts. One gram of the tantalum salt dissolves in 150 grams of water while an equal weight of the niobium salt requires only 12 parts water.

A method presented by Schoeller (5) makes use of the different extents to which tantalum and niobium oxalates are affected by hydrolysis. Tannin

precipitates the tantalum complex from a slightly acid solution while an excess of tannin precipitates niobium from a neutral solution. This method is commonly used for analytical procedures and it does not appear to be practical for a large scale operation.

Besides the sodium hydroxide fusion mentioned earlier, many other alkaline and acidic fluxes are used to open the ore for analytical determinations. Schoeller (5) has discussed these fluxes in great detail. For analytical determinations Schoeller recommended the use of an acid flux, potassium bisulfate. Alkaline fluxes were considered undesirable because of unavoidable contamination of the melt with the material of the crucible. From an economic standpoint these fluxes are undesirable for commercial operation because of their cost and the high weight ratio of flux to ore (10-20:1) to effect a good recovery. Pierret (8) has adequately reviewed the various fusion processes attempted for the opening of the ore.

Generally the actual separation of tantalum and niobium has been accomplished after most all of the impurities have been removed by a fusion and chemical processing procedure. Several investigators have tried separations without involving a fusion step. Jenness (9) obtained tantalum and niobium from ore by chlorinating each metallic element in the ore and raising the temperature to the volatilization point of each chloride.

May, Henderson and Johansen (10) described a method for separating tantalum and niobium by selective chlorination which followed a heat treatment of partially hydrolyzed tantalum and niobium chlorides with ammonia or ammonium chloride. This method was only applied to pure mixtures

of the oxides. Separation was not quantitative and depending upon conditions of hydrolysis only one purified component of the mixture was obtained. Hiskey and co-workers (11) volatilized niobium and tantalum by treating the oxide mixture with a chlorinated hydrocarbon. This method was not applicable to ores as the presence of iron caused catalytic decomposition of the chlorinating agent. Recently, however, it was reported (12) that the addition of two to four per cent sodium chloride promotes the formation of stable nonvolatile ferric chloride complexes during the chlorination of niobium-tantalum ores. This particular chlorination method was proven on Western Black Sand deposits by the Bureau of Mines. Heating the chlorination charge to 500° C. for one hour first distilled off titanium tetrachloride and then niobium and tantalum chlorides. These latter were condensed separately by selective hydrolysis as reported above (10). Iron carryover is cut from 60 per cent to practically nil.

Curvellier (13) patented a process whereby niobium was separated from tantalum by roasting the ore in air at about 800 to 1200° C. with a basic substance which was usually calcium oxide. The residue from the roasting process was heated in a chlorine atmosphere at 800 to 1050° C. for several hours. Seventy to 80 per cent of the niobium was volatilized as a chloride-oxychloride mixture while practically all the tantalum remained in the residue.

Lind and Ingles (14) reported 99.8 per cent recovery of niobium from niobium ores by chlorination with chlorine gas. Niobium oxychloride or pentachloride was recovered depending upon the conditions of the reaction.

The niobium produced was free from the gangue materials iron and manganese. No report was made on tantalum.

Ruff and Thomas (15) reported using carbon tetrachloride as a chlorinating agent in the treatment of tantalum and niobium oxides. At 200 to 225° C. niobium pentachloride was formed, while the tantalum oxide remained unaffected. No sharp separation occurred, however, as in a secondary reaction, niobium pentachloride reacted with tantalum oxide to give niobium oxychloride and tantalum pentachloride.

Kroll and Bacon (16, 17) also patented a process for selective chlorination. More niobium oxide than tantalum oxide formed a nitride when the mixture was treated with ammonia at 600° C. When chlorine was passed over this partially nitrided mixture at 500° C. niobium was fractionally distilled. In one test 88 per cent of the niobium and less than 5 per cent of the tantalum were removed from a mixture initially composed of 47 per cent niobium oxide and 53 per cent tantalum oxide. Other patents (18, 19) suggested treatment of the mixed oxides with hydrogen to reduce selectively the niobium pentoxide to the tetroxide. After this partial reduction, the charge was treated with chlorine gas to distill niobium pentachloride. Only about 20 per cent of the niobium was removed in one cycle.

A French patent (20) described a process for separating tantalum and niobium. Mixed oxides were added to a fused alloy containing tantalum and niobium. Tantalum in the alloy was displaced with respect to niobium producing a slag containing tantalum and an alloy containing niobium.

Golibersuch and Young (21) precipitated niobium containing less than 0.2 per cent tantalum by electrolytic reduction of quinquevalent niobium to the quadri- and trivalent states in a 75 per cent sulfuric acid solution. In a similar process (22) niobium was reduced in acid solution with zinc dust. Boiling precipitated the tantalum hydrate, leaving the lower valent niobium in solution. The niobium was then reoxidized and precipitated by boiling.

Yntema (23) reported that an incomplete separation could be effected by electrolytic hydrolysis with different hydrogen ion concentrations. Later investigations by Pierce and Yntema (24) indicated that it was impossible to effect a clean separation by merely regulating the pH. Later, Pierce (25) claimed that niobium could be plated from a saturated solution of ignited niobium oxide in sodium carbonate. A similar solution of tantalum oxide would not plate out tantalum under identical conditions.

Anion-exchange methods have been found effective in separating tantalum and niobium. One method employing a mixed hydrochloric-hydrofluoric acid solution of niobium and tantalum indicated that tantalum was preferentially adsorbed (26, 27). Huffman and co-workers (28) found niobium preferentially adsorbed from hydrochloric acid solutions. The niobium and tantalum obtained by these ion-exchange techniques were better than 99 per cent pure relative to each other. Gillis and co-workers (29) recovered 95 per cent of the niobium free of tantalum by one pass of their oxalic acid solution containing equal weights of the two elements.

Several successful chromatographic separations of niobium and tantalum

have been reported. Burstall and associates (30, 31) charged cellulose with a fluoride solution of niobium and tantalum and then elutriated this with methyl ethyl ketone. The tantalum was quantitatively transferred to the ketone and was found to contain as little as 0.1 per cent niobium. Addition of hydrofluoric acid to the eluant was required to remove the niobium from the cellulose. Tikhomiroff (32) accomplished this same separation by adsorption on activated alumina from an ammonium oxalate solution. Wood (33) added ammonium ion to the fluoride solutions of niobium and tantalum poisoned with a little titanium. Adsorption on cellulose followed by elutriation showed the ammonium ion completely surpressed the transfer of the titanium. This is a significant factor in the preparation of pure niobium as titanium usually associates itself with the niobium.

Recently, separations have been achieved by liquid-liquid extraction methods. Leddicotte and Moore (34) found that a solution of methyldi-octylamine in xylene extracted about 99 per cent of the niobium and only 0.8 per cent of the tantalum from an 8.0 molar hydrochloric acid solution. Scadden and Ballou (35) reported only partial separation by preferentially extracting niobium from a nitric acid solution of their oxalates into a 0.6 molar solution of di-n-propyl phosphoric acid in dibutyl ether. Stevenson and Hicks (36) effected a separation by extraction of tantalum into diisopropyl ketone from mineral acid-hydrofluoric acid aqueous phases. The mineral acids tested were hydrochloric, sulfuric, perchloric and nitric. Hydrochloric acid was reported to be most useful. All of the above extractions were carried out on aqueous solutions containing less than 2.5 grams each of tantalum and niobium per liter.

Ellenburg, Leddicotte and Moore (37) extracted niobium from tantalum as a sulfate with a mixed solvent of tribenzylamine in methylene chloride. Werning and associates (38, 39) obtained 99.85 per cent tantalum and 99.97 per cent niobium with the hydrofluoric acid-hydrochloric acid-methyl isobutyl ketone systems. West (40) has reviewed the above extraction papers in fair detail.

Wilhelm, Kerrigan and Cass (41) reported that many organic solvents were capable of preferentially extracting tantalum from a hydrofluoric acid solution containing high concentrations of niobium and tantalum. In furthering this work Foos and Wilhelm (42) studied the effects of varying the concentration of niobium, tantalum and hydrofluoric acid on the extraction. An aqueous solution containing the equivalent of 517 grams of tantalum and niobium pentoxides per liter was used in these experiments. Single stage extractions of this solution or its water dilutions with many organic solvents indicated that some solvents extracted more than 50 per cent of the total tantalum analyzing less than one per cent niobium. Although the ketones were most effective for obtaining the separation, many alcohols, amines, aldehydes, ethers, esters, organic phosphates, organic phosphites and mixed organic solvents were useful. A multiple-contact batch extraction carried out on a solution containing 110 grams per liter of total oxides with diethyl ketone gave in three stages a 99 per cent recovery of the tantalum which analyzed about 0.15 per cent niobium. The most effective separation of tantalum from niobium was obtained when the free hydrofluoric acid content was low.

Other less corrosive systems were also investigated for separating tantalum from niobium by liquid-liquid extraction. Extraction of hydrofluoric acid solutions of niobium and tantalum which had been partially or completely neutralized with aliphatic or aromatic hydroxyamines indicated favorable mass distribution and separation of tantalum from niobium. Tantalum preferred the organic phase in these systems. Although the same general extraction trends were observed for the amine-free and the amine-neutralized hydrofluoric acid solutions of niobium and tantalum, the former system gave higher degrees of separations. Niobium was preferentially extracted by the organic phase from a potassium hydroxide solution of niobium and tantalum. However, in this system the mass transfer and degree of separation were low.

Several counter-current multistage extractions were carried out in which diethyl ketone was employed as the organic phase and amine-neutralized hydrofluoric acid solution of niobium and tantalum as the aqueous phase. In from 10 to 15 stages tantalum and niobium spectrographically free of each other were obtained quantitatively on a continuous basis.

INVESTIGATION

It was the objective of this investigation to develop a process for the production of spectrographically-pure niobium and tantalum oxides. The general form of the process is shown in Figure 1. It was necessary to develop methods for carrying out the individual steps in the process and to determine operating conditions and chemical and equipment requirements.

The investigation was divided into five sections: (a) opening of the ore, (b) preparation of the extractor feed solution, (c) separation of niobium and tantalum, (d) solvent treatment and recovery, and (e) final conversion of products.

Opening of the Ore

The source material for the earth oxides was a columbite ore concentrate from Nigeria. The analysis of the ore used in this investigation was made by the Ledoux Company and is shown in Table 3.

The ore concentrate, as received, was mostly retained on a 65 mesh Tyler screen. Initial experiments on this "as received" ore indicated that a smaller particle size was necessary for reasonable reaction rates. The ore concentrate was then ground to pass 325 mesh in a Raymond hammer mill pulverizer.

Table 3. Ledoux analysis of Nigerian columbite ore

Constituent	Per cent
Nb_2O_5	61.93
Ta_2O_5	6.80
FeO	18.65
MnO	1.51
TiO_2	3.48
SnO_2	2.86
H_2O	0.01
	95.24

Acid dissolution of columbite ore

The columbite ore concentrate could be dissolved in sulfuric or hydrofluoric acids, but in order to obtain economical separation of niobium and tantalum the final feed solution must be niobium and tantalum fluoride. Each acid was tested in some detail and the resulting procedures compared. It was desirable to eliminate filtration steps since experience with the fusion process showed that filtrations of various niobium and tantalum salts were extremely troublesome.

Dissolution of columbite ore in concentrated sulfuric acid was only moderately successful. Employing an acid to ore weight ratio of five to

one and heating at 300° C. for one-half hour yielded 50 to 70 per cent reaction of the ore. When the sulfuric acid-columbite ore reaction mass was diluted approximately fifteen fold with water, niobic and tantalic acids (commonly called earth acids) were precipitated while the iron and other gangue materials of the ore went into solution as sulfates. Filtration of the earth acids and unreacted ore was very troublesome because of the gelatenous nature of the cake. If the reaction mass were filtered before dilution and then the filtrate and cake diluted with water separately, two earth acid fractions could be obtained. The fraction recovered from the filtrate dilution was approximately 90 per cent niobium while the fraction from the cake assayed 80-90 per cent tantalum. The starting columbite ore for the above experiment was an Argentina ore which assayed 50 per cent Nb_2O_5 and 17 per cent Ta_2O_5. However, this procedure doubled the filtration difficulty because both cakes were again very gelatenous.

It was first determined by Wilhelm (43) that niobium-tantalum ores could be successfully opened by hydrofluoric acid. Wilhelm's tests indicated that 90 per cent reaction of the ore was possible when a 100 per cent excess of cold 70 per cent hydrofluoric acid was shaken with ore concentrate for 8-12 hours.

Dissolution of the ore concentrate in hydrofluoric acid was attractive because of the direct conversion to the desired niobium and tantalum fluorides. However, excess hydrofluoric acid was known to decrease separation factors in the extraction process and hence was undesirable. Hydrofluoric acid requirements for the Nigerian columbite ore were calculated and are

Table 4. Seventy per cent hydrofluoric acid requirements of Nigerian columbite ore

Basis: 100 grams ore

Constituent		Weight		Weight 70 per cent hydrofluoric acid
as oxide	as fluoride	as oxide	as fluoride	
Nb_2O_5	H_2NbOF_5	61.93	95.95	66.57
Ta_2O_5	H_2TaF_7	6.80	9.73	3.09
FeO	FeF_2	18.65	24.36	14.83
MnO	MnF_2	1.51	1.98	1.21
TiO_2	TiF_4	3.48	5.40	4.99
SnO_2	SnF_4	2.86	3.70	1.09
H_2O	--	0.01	---	---
		95.24	141.12	91.78

shown in Table 4.

As can be seen from Table 4, 100 grams of this particular columbite ore required approximately 92 grams of 70 per cent hydrofluoric acid. Since about five per cent of the ore was unaccounted for by the Ledoux analysis, it was arbitrarily decided to increase the requirements to a one to one weight ratio.

Experiments were run to verify Wilhelm's results. The first tests indicated that even with a large excess of hydrofluoric acid, the reaction

mass was viscous. Diethyl ketone was added to increase the fluidity of the reactants. The results obtained are shown in Table 5. It should be noted here that the hydrofluoric acid concentration in all of the following work was 70 per cent unless otherwise stated. Henceforth, when hydrofluoric acid is mentioned, the 70 per cent variety is inferred.

Table 5. The effect of diethyl ketone on the hydrofluoric acid-columbite ore reaction

Ore grams	Hydrofluoric acid		Diethyl ketone milliliters	Per cent reaction	Hours of reaction
	milliliters	per cent			
10	15	75	25	79.5	12
10	15	75	--	92.4	12
10	10	25	25	68.8	23
10	10	25	--	90.4	23
10	7.5	0	25	55.9	23
10	7.5	0	--	81.7	23

The columbite ore in the previous experiments was the Argentina ore. Hydrofluoric acid requirements for this ore were such that 7.5 milliliters was necessary for ten grams. Also, it is noted here that diethyl ketone was used in many of the early experiments. A plentiful supply was at hand and since it belonged to the same class of compounds as hexone, it was considered immaterial which was actually used.

The results of Table 5 showed that the presence of diethyl ketone decreased the amount of reaction. Apparently the diethyl ketone acted as a diluent. It was also apparent that excess hydrofluoric acid was necessary for economical reaction rates. The solutions containing the diethyl ketone were more easily filtered than the solutions containing only hydrofluoric acid. Furthermore, only one phase was noted which indicated the diethyl ketone had extracted the hydrofluoric acid and the niobium and tantalum fluorides. Neutralization of a portion of the organic ketone product resulted in the precipitation of relatively pure niobium and tantalum oxides (commonly called earth oxides). Earth oxides recovered from the aqueous solutions were colored brown instead of the usual white. The brown color was caused by iron and other impurities in the oxides. It appeared that the extraction of the niobium and tantalum fluorides into an organic solvent after the ore had been reacted with hydrofluoric acid would result in a simple procedure for eliminating the gangue materials of the ore.

In a second series of experiments various mixtures of hydrofluoric acid and concentrated sulfuric acid were reacted with 10 grams of columbite ore. It was thought that the sulfuric acid would react with the various fluorides as they formed to generate more hydrofluoric acid for attacking the ore. The results of this experiment are shown in Table 6.

The results of Table 6 showed that the presence of another liquid again acted as a diluent for the hydrofluoric acid. Direct comparison of the results in which 75 per cent excess acid was used revealed that sulfuric acid decreased the amount of reaction as much as ten per cent as compared

Table 6. Effect of sulfuric acid on the hydrofluoric acid treatment of columbite ore

Ore grams	Hydrofluoric acid milliliters	Hydrofluoric acid per cent excess	Sulfuric acid milliliters	Per cent reaction	Hours of reaction
10	20	146	20	86.3	11
10	20	146	20	88.0	14.5
10	15	75	25	81.9	11
10	15	75	25	84.4	14.5
10	10	25	30	79.0	11
10	10	25	30	81.0	14.5
10	7.5	0	32.5	--	11
10	7.5	0	32.5	70.9	14.5

to when no diluent was added. On the other hand, sulfuric acid dilution resulted in three to five per cent more reaction than when diethyl ketone was the diluent.

Addition of sulfuric acid to the reaction mass of hydrofluoric acid and columbite ore eliminated the possibility of extracting the earth acid fluorides from the reaction mass with an organic solvent. The large amount of sulfuric acid resulted in two liquid phases when diethyl ketone was added. Phase separation was poor and made recovery of the unreacted ore residue and the earth acids impossible. The blank space in Table 6 was

Table 7. Reaction of Nigerian columbite ore with anhydrous hydrofluoric acid

System	Time of run hours	Temperature ^{o} C.	Per cent reaction
Closed	0.5	100	43
Closed	1.0	200	70
Open	4.0	200	0
Open	4.0	500	0
Open	6.0	800	10

the result of following this procedure. Attempts to reduce the amount of sulfuric acid were not successful. As long as any sulfuric acid was present, two phases were obtained when diethyl ketone was added to the reaction mass.

Attempts were made to react columbite ore with anhydrous hydrofluoric acid in both sealed and open systems. A sealed bomb reactor and a rotary kiln type furnace were used in these experiments. The conditions and results of these experiments are shown in Table 7.

As can be seen from Table 7, the reaction of columbite ore and anhydrous hydrofluoric acid worked better in a closed system than in an open system. The reaction rates shown for the closed system probably could have been higher. Stains on the lead gasket indicated hydrofluoric acid loss. Also, no fumes of hydrofluoric acid were noted when the closed

reactors were opened. For the open reactions no weight loss was noted in the first two cases reported. Leaching of the ore after reaction with both water and hexone resulted in no oxide recovered. It was concluded from these tests that a gaseous hydrofluoric acid-columbite ore reaction was feasible but only when it was run under pressure in a closed reactor.

Dissolution of the columbite ore in hot 70 per cent hydrofluoric acid was found to be the most desirable method tested. A Fluorethene beaker and cover were used in these experiments. A stirrer rod and paddle were fabricated from rigid polyvinyl chloride, sold under the trade name "Lucoflex", and was inserted through a small hole in the center of the cover. The heat source was a hot plate calibrated to continuously operate at 100° C.

Aqueous 70 per cent hydrofluoric acid was added to the ore concentrate and allowed to react for various lengths of time, forming a slurry of fluorides and unreacted ore. At the end of the reaction period hexone was added to the slurry to extract the niobium and tantalum fluorides. The solution was allowed to cool and was then filtered in a polyethylene buchner funnel to remove the solids and produce a clear filtrate. The fluoride cake was washed countercurrently with hexone solutions from previous reactions, the last wash being fresh hexone acidified to one normal with hydrofluoric acid.

In order to use the hydrofluoric acid most effectively, it was decided to add an excess of ore to the reaction vessel. It was hoped that this method of operation would reduce loss of the acid by volatilization and also tend to keep the free hydrofluoric acid content of the hexone solution

Table 8. Reactions of 70 per cent hydrofluoric acid and columbite ore at 100° C.

Run number	Acid/ore weight ratio	Time of run hours	Per cent reaction
2	0.8	1	46.0
3	0.8	2	65.0
4	0.8	4	94.8
5	0.8	4	94.8
6	0.8	4	90.6
7	0.8	4	88.0
8	0.8	4	70.3
9	0.8	4	76.1
10	0.9	4	72.8
11	1.2	93	99.3
12	0.8	9	90.7
13	1.1	12	99.0

as low as possible. In the first experiments 82 milliliters of 70 per cent hydrofluoric acid were reacted with 125 grams of columbite ore. This ratio of acid to ore was such that a 25 per cent excess of ore was present. The results of these and later experiments under other conditions are presented in Table 8. The amount of reaction was determined by dissolving the filter cake in water and/or acid and weighing the unreacted ore.

The data in Table 8 show that four hours was apparently a reasonable reaction time. Undoubtedly, some hydrofluoric acid was lost by volatilization under the conditions employed. It is believed safe to assume, then, that a reaction time of four hours in a suitable vessel, designed to eliminate hydrofluoric acid losses, would give nearly a complete reaction of the ore. The low values reported in runs 7-10 were the result of dissolving the cake in water alone. Some fluoride residue was noted in the unreacted ore from these runs so that the per cent reaction was probably higher. For the basis of future calculations, a reaction time of four hours and a 100 per cent opening of the ore will be used. Volume requirements for the reaction vessel were determined to be 0.192 gallons per pound of ore processed.

Preparation of the Extractor Feed Solution

In general the source materials for niobium and tantalum contained about 20 per cent total iron and manganese and roughly five per cent tin and titanium. In order that final purity of the niobium and tantalum be high, it was necessary to eliminate these foreign materials as early as possible in the extraction procedure. Early experiments utilizing aqueous feed solutions showed iron to be present in tantalum to the extent of 0.25 to 0.50 per cent. The elimination of titanium was especially desirable since it associated itself with niobium and its removal necessitated a separation which is achieved with great difficulty.

Countercurrent leaching with hexone

Direct filtration of the hydrofluoric acid-columbite ore reaction mass resulted in incomplete recovery of the niobium and tantalum fluorides. Complete recovery was effected when the filter cake was washed with water but this procedure also dissolved the iron, manganese, titanium, and tin fluorides which contaminated and diluted the original solution. Washing the aqueous fluoride cake with hydrofluoric acid was moderately successful but this scheme proved uneconomical as the hydrofluoric acid requirements became excessive.

Leaching the reaction mass with hexone proved to be the most effective method tested. Four countercurrent leaches were employed for each reaction mass. The final leach in each case was either fresh hexone or hexone acidified to one normal with hydrofluoric acid.

The first leach was made by mixing the second leach solution from a previous run directly with the reaction mass. The slurry was then filtered to apparent dryness on a polyethylene buchner funnel. In all cases the first leach resulted in recovering 70 per cent or more of the niobium-tantalum fraction of the ore. The filtrate volume from the first leach increased 25 per cent over the amount of hexone originally added. No significant increases were noted in any of the volumes of the following three leaches. The second leach was made by transferring the filter cake back to the reactor and mixing thoroughly with the third leach solution from a previous run. This solution usually contained about 16 per cent of the

niobium and tantalum. Repeating the above procedure for the third leach resulted in a solution containing 6-7 per cent of the niobium and tantalum.

When the fourth leach was made with fresh hexone, very little niobium and tantalum was found in the filtrate. However, if the fresh hexone were first acidified to one normal with hydrofluoric acid, 2-3 per cent more of the niobium and tantalum was recovered.

Filtration difficulties ceased when the hexone leach procedure was used. Attempts to filter the aqueous reaction mass failed as the cake set up on the filter before complete recovery of the liquid could be effected. Filtering the reaction mass hot eliminated some of this difficulty but the problem of recovery still remained.

When the first organic leach solution was filtered, the solids always came out of the reactor intact. This first filter cake resembled a piece of gelatin until all of the liquid was removed. Subsequent filter cakes were then very granular in nature and filtered with great ease. The color of the filter cakes progressed from a dark brown after the first filtration to a light tan after the final filtration.

Detailed filtration studies were not conducted on the above filter cakes. The characteristics of the cakes were such that high filtration rates were always effected and hence a detailed study was not necessary. Each filter cake was filtered four times, once after each washing. By calculation, a filter area of 0.791 square feet per pound of ore processed based on a cake thickness of one inch was determined necessary.

The washing or leaching of the filter cake was determined to be an important part of the process. Countercurrent washing, as carried out on the bench scale, repeatedly yielded recovery of 95-96 per cent of the niobium and tantalum in the ore. To yield the same results on a larger scale, it was determined that a filter such as the Bird Prayon or Eimco Pan would be necessary. These filters have the reputation of high cake washing efficiency and sharp separation of filtrates, two features which fit in well with the proposed procedure. Because of the corrosiveness of hydrofluoric acid and the toxicity and inflammability of hexone, such a filter would be completely enclosed. The whole unit could be constructed of monel but a cheaper method would be to employ plastics and plastic coatings. Before any material of construction is chosen, it is recommended that corrosion tests be made.

The wet cake contained 0.18-0.20 pounds of hexone per pound of solids. For economical operation this hexone should be recovered. Drying of the fluoride cake was not investigated.

Separation of Niobium and Tantalum

Conditions for the separation of niobium and tantalum were determined by simulated column runs. Both diethyl ketone and hexone were used in these runs. Nine simulated column runs were made under varying conditions. In all cases the niobium and tantalum were present with excess hydrofluoric acid in the organic phase. Various concentrations of sulfuric acid were tested as the aqueous scrub solution. The tantalum preferentially remained

in the solvent while the niobium and minor impurities were scrubbed into the aqueous raffinate.

Single stage extractions with hexone

Single stage liquid-liquid extractions were used to obtain distribution coefficients of pure tantalum and pure niobium in hydrofluoric acid solutions with hexone. Two primary stock solutions of tantalum were made by dissolving tantalum oxide, in one case, and tantalum metal, in the second case, in hydrofluoric acid. The solution made from the tantalum oxide analyzed 595 grams oxide per liter while the solution made from the tantalum metal analyzed 1176 grams oxide per liter. A third tantalum stock solution was made by adding hydrofluoric acid to a portion of the second tantalum solution. This stock solution, which analyzed 989 grams oxide per liter, was an attempt to prepare a solution one normal in excess hydrofluoric acid. All of these solutions remained stable for over a year. A primary stock solution of niobium was made by dissolving niobium oxide in hydrofluoric acid. This solution assayed 598 grams oxide per liter. A portion of the niobium solution was evaporated yielding a second stock solution of 852 grams oxide per liter. The niobium stock solutions were unstable as precipitation started a few days after preparation. These stock solutions and various water dilutions were used as feed solutions for the single stage extractions.

Extractions were made by shaking equal volumes of feed solution and virgin hexone in a polyethylene container. All shake ups were made for two

minutes even though no further changes in distribution were noted after 30 seconds. The phases were then separated in a polyethylene separatory funnel and stored in polyethylene bottles for analysis. The analytical procedures used are discussed in Appendix A.

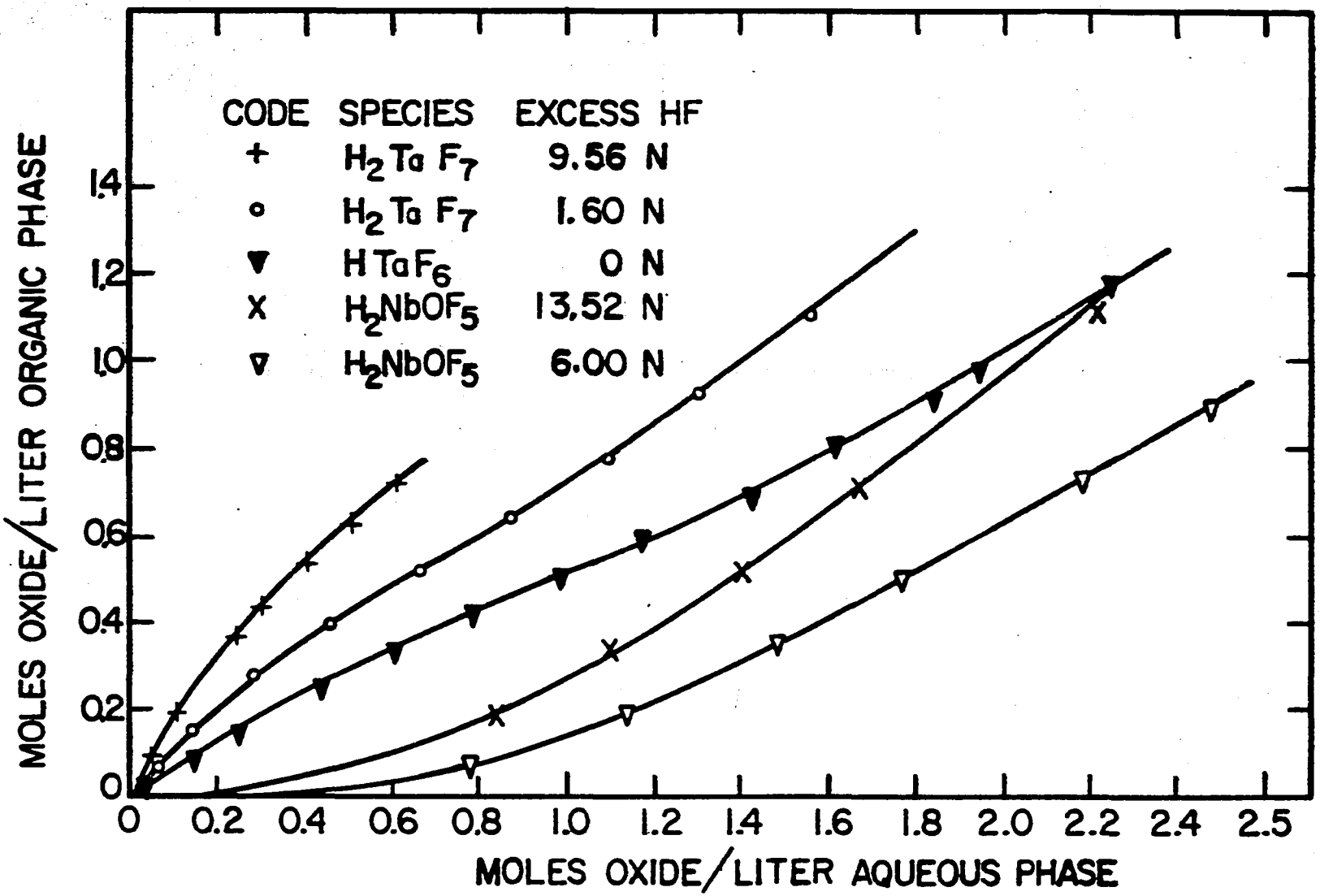
Distribution data for the three tantalum stock solutions and the two niobium stock solutions are shown in Figure 2. The concentrations in Figure 2 are shown in moles per liter to allow for more direct comparison. The data for these curves are tabulated in Table 22 in Appendix B.

An accurate determination of the excess hydrofluoric acid concentration was desired for the primary stock solutions. The best procedure found for the excess hydrofluoric acid concentration was by the determination of the fluoride ion by a modified Willard and Winter (44) analysis. This method was found satisfactory on standard solutions of tantalum and niobium in hydrofluoric acid and is presented in Appendix A.

Figure 2 shows that an increase in excess hydrofluoric acid concentration increased both the tantalum and niobium distribution coefficients. It is also apparent that the niobium distribution is more affected by an increase in acid concentration than is the tantalum. Foos (45) has presented a possible explanation for the lack of preferential extraction of tantalum at higher hydrofluoric acid concentrations by the following reactions.

$$7\ HF + H_3TaO_4 \rightleftharpoons H_2TaF_7 + 4H_2O \qquad (1)$$

Figure 2. Distribution curves for pure niobium and tantalum fluorides with hexone


CODE SPECIES EXCESS HF
+ H_2TaF_7 9.56 N
○ H_2TaF_7 1.60 N
▼ $HTaF_6$ 0 N
X H_2NbOF_5 13.52 N
▽ H_2NbOF_5 6.00 N
MOLES OXIDE/LITER ORGANIC PHASE
0 0.2 0.4 0.6 0.8 1.0 1.2 1.4
MOLES OXIDE/LITER AQUEOUS PHASE
0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.5

$$5HF + H_3NbO_4 \rightleftharpoons H_2NbOF_5 + 3H_2O \qquad (2)$$

$$2HF + H_2NbOF_5 \rightleftharpoons H_2NbF_7 + H_2O \qquad (3)$$

The products of reactions 1 and 3 are very similar while the niobium and tantalum salts from reactions 1 and 2 are quite different. It would be expected that the relative extractability of fluotantalates and the fluoniobiates might be similar while for the fluotantalates and the pentafluoniobiates it might be different. Thus if an amount of hydrofluoric acid insufficient to yield appreciable amounts of reaction 3 were present, considerable difference in niobium and tantalum extractability should result.

A research paper by Werning and associates (38) also reported data on the extractability of tantalum and niobium at various hydrofluoric acid concentrations. This work showed that tantalum extractability apparently reached a maximum at about six normal hydrofluoric acid while the extractability of niobium continued to increase at hydrofluoric acid concentrations as high as 15 normal.

Figure 2 also revealed that an increase in concentration also increased the distribution coefficient of both tantalum and niobium. However, it is interesting to note that the niobium distribution coefficient apparently increased until the aqueous solution was approximately one molar and then remained constant. This same effect is also noted for the tantalum distribution coefficient until the aqueous solution was approximately 0.5 molar.

The middle curve on Figure 2 presented an interesting topic for discussion. The fluoride ion determination revealed that the species $HTaF_6$ was present with no excess hydrofluoric acid. The proximity of this curve to the other tantalum curves showed that $HTaF_6$ was not as extractable as H_2TaF_7. It has been suggested many times that tantalum and niobium fluorides are extracted by ketones through hydrogen bonding. If this be the case then, it follows that the $HTaF_6$ species is not as extractable as H_2TaF_7 because of the deficiency of hydrogen.

Simulated column runs using diethyl ketone

A diethyl ketone solution containing 209 grams oxide per liter and assaying 41.8 per cent tantalum oxide and 58.2 per cent niobium oxide was used in the following tests. A fluoride determination also showed this solution to be three normal in excess hydrofluoric acid.

Since the distribution coefficient of niobium increased more than the distribution coefficient of tantalum at increased concentrations, it would be expected that the separation factors would increase with decreased niobium-tantalum concentrations. To check this conclusion a series of one stage extractions were made with the above diethyl ketone solution. One molar sulfuric acid was employed as the aqueous phase in this test. The results of these one stage shake ups are shown in Figure 3 and Table 9.

Figure 3 shows that the tantalum-niobium separation factor increased very rapidly when the initial feed concentration was decreased below 100 grams oxide per liter. However, even at concentrations above 200 grams

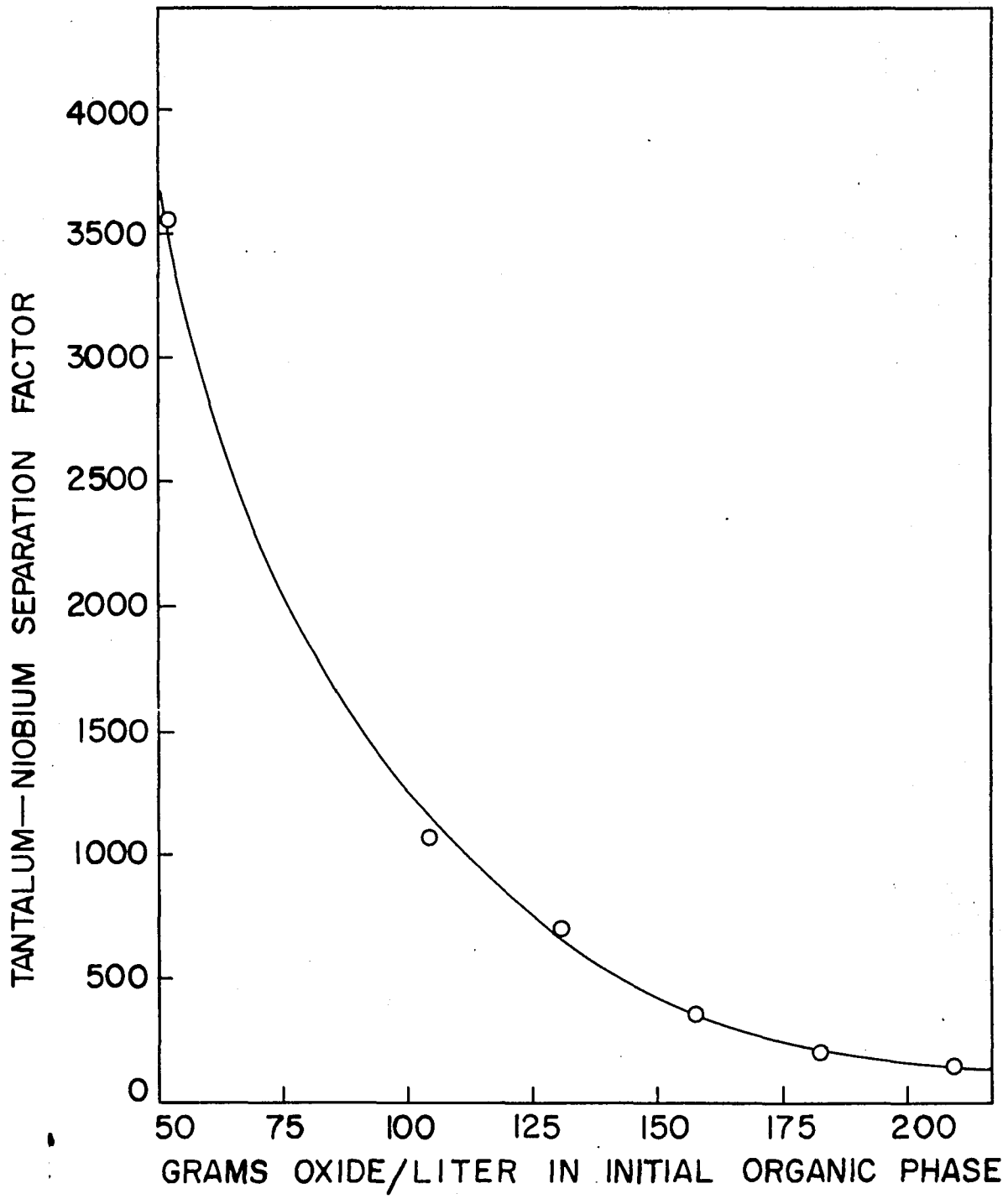


Figure 3. Effect of initial feed concentration in diethyl ketone on tantalum-niobium separation factors

Table 9. Equilibrium contacts with varying oxide concentration in diethyl ketone and one molar sulfuric acid

Conc. of feed (grams oxides/l)	Organic phase				Aqueous phase				K_{Ta}	K_{Nb}	β
	Grams oxides/l	Per cent Ta_2O_5	Grams Ta_2O_5/l	Grams Nb_2O_5/l	Grams oxides/l	Per cent Nb_2O_5	Grams Ta_2O_5/l	Grams Nb_2O_5/l			
209	113.4	91.04	103.2	10.2	100.2	92.87	7.2	93.4	14.4	0.109	132
183	98.6	90.05	88.8	9.8	87.2	95.59	3.8	83.4	23.0	0.118	196
157	80.6	92.02	74.2	6.4	69.7	96.78	2.2	67.5	33.1	0.095	347
131	66.8	94.47	63.1	3.7	63.6	97.57	1.6	62.0	40.7	0.059	685
104.5	51.2	95.11	48.7	2.5	49.6	98.20	0.9	48.7	54.7	0.051	1066
52.3	24.9	96.76	24.1	0.8	24.1	99.15	0.2	23.9	120.5	0.034	3554

oxide per liter, a separation factor of over 130 was present.

It can be seen from Table 9 that all of the organic phases analyzed 90 per cent or more tantalum oxide. Similarly all of the aqueous phases contained 90 per cent or more niobium oxide. In view of the high separation factors obtained, this phenomenon was to be expected.

A method for predicting the separation of niobium and tantalum by liquid extraction was desired. Since the organic phase was tantalum-rich and the aqueous phase was niobium-rich after only one contact, it was thought that the pure component curves from Figure 2 could be used for this prediction. However, no completely successful method was found.

Tantalum distribution coefficients calculated from Figure 2 were usually less than one. It can be seen from Table 9 that the tantalum distribution coefficients ranged from 14 to 120. It appeared that at lower excess hydrofluoric acid concentration the niobium acted as a salting out agent for the tantalum which necessarily increased the tantalum distribution coefficient. This salting out effect is also apparently more pronounced when the feed concentration is decreased.

Since the system sulfuric acid-tantalum and niobium fluorides-diethyl ketone was too complicated for calculation of stage requirements for equilibrium data by standard methods, extraction stages were determined empirically by a series of simulated column extractions. These simulated columns were used to provide the same data as a countercurrent extraction by the use of polyethylene separatory funnels as extraction stages. The

flow pattern was arranged to simulate countercurrent flow of solvent and sulfuric acid.

A fractional extraction technique was used in which the feed was introduced at an intermediate point in the extractor. The organic solvent and an aqueous scrub solution were fed to opposite ends of the extractor.

In the analysis of the extraction operation the mixer-settler was divided into extraction and scrub sections. The region between the solvent entry point and the feed stage was taken as the extraction section. The action of the solvent was to reduce the amount of tantalum leaving in the raffinate solution. In the feed stage essentially all of the niobium along with some tantalum was transferred to the scrub solution entering the extraction section. The function of the extraction section was to prevent any of the tantalum from leaving the extraction unit in the raffinate. The entering solvent progressively extracted the tantalum and niobium from the aqueous phase and carried back to the feed stage all the tantalum leaving the feed stage. Since the solvent preferentially extracted tantalum, the aqueous phase grew progressively richer in niobium although both materials were being transferred to the solvent. Thus a tantalum-free niobium concentrate left the extractor in the aqueous phase, or raffinate.

The scrub section was defined as the region from the solvent entry to the feed stage. The solvent entering the scrub section came from two sources, the feed and the organic solution from the extraction section. The action of the scrub solution was to progressively decrease the relative

concentration of niobium in the solvent since the scrub solution preferentially extracted niobium. Thus as the solvent passed through the scrub section, both niobium and tantalum were transferred to the scrub solution, but the preferential action of the scrub removed relatively more niobium, leaving niobium-free tantalum in the exit solvent phase.

Five simulated column runs were made with the diethyl ketone feed solution. The apparatus used in these simulated column runs was unique and warrants a short description. The mixing and separatory funnels were made from ordinary polyethylene "Tupperware" 16 ounce cups. A one inch piece of three-eights diameter polyethylene tubing was welded to the bottom of each cup. A hole was bored through the bottom of the cup to coincide with the inside diameter of the tubing. Another short piece of tygon tubing was firmly attached to the polyethylene tubing. Pinching the tygon tubing with a pinch clamp provided an effective stopcock. A corrosion resistant stirrer was made by welding a polyethylene paddle to a polyethylene coated stainless steel rod. A thin sheet of polyethylene was used to cover each mixing tube to minimize losses by volatilization and splashing.

The first extraction test was made in an eight stage simulated column under the following conditions:

Feed: 30 milliliters of diethyl ketone feed solution added at stage five.

Scrub: 120 milliliters of one molar sulfuric acid added at stage

one.

Organic: 30 milliliters of diethyl ketone added at stage eight.

This type of operation gave five scrub stages with an organic (O) to aqueous scrub (A) volumetric flow rate ratio of 1/2 and three extraction stages with O/A = 1/4.

After twenty-nine cycles the run was stopped and the column was sampled stagewise. This data are presented in Table 10. The aqueous product from stage eight analyzed >99.93 per cent niobium oxide or less than 700 parts per million (ppm) tantalum oxide which was the limit of detection of tantalum oxide. The organic product from stage one analyzed approximately 99.95 per cent tantalum oxide. The limit of detection was 100 ppm niobium oxide in tantalum oxide and it was concluded that separation was not totally effected under these conditions.

Since the organic product contained about 500 ppm niobium, expressed as oxides, instead of less than 100 ppm as desired, other operating conditions were studied in an attempt to produce purer tantalum. It was noted in Table 10 that the aqueous streams from stages seven and eight contained spectrographically pure niobium. This indicated that stage eight was not necessary to the extractor. It was also noted that the compositions of the organic phases in stages one through four remained essentially constant in tantalum content. Similarly the compositions of the aqueous phases in stages one through three remained constant. This indicated very little separation was occurring. A check of the separation

Table 10. Stagewise analyses for the first niobium-tantalum simulated column run using diethyl ketone

Stage number	Organic phase			Aqueous phase		
	Volume (ml)	Grams oxide/ liter	Per cent Ta_2O_5	Volume (ml)	Grams oxide/ liter	Per cent Nb_2O_5
1	23.25	60.82	99.95	62.0	12.85	0.10
2	23.5	83.22	99.95	60.0	20.23	0.10
3	26.5	94.30	99.95	64.5	23.00	0.10
4	24.0	104.0	99.95	62.6	17.18	0.76
5	26.5	83.70	66.73	65.0	28.08	98.02
6	14.0	24.24	96.09	63.0	22.95	99.00
7	14.5	4.61	43.17	65.0	21.73	>99.93
8	14.0	2.88	0.01	62.0	21.22	>99.93

factors for the first three stages confirmed this fact. Separation factors of 1.5-2.7 were calculated for the first three stages while this factor increased rapidly to 77.5 in stage four and 98.5 in stage five.

The data of Table 10 also revealed that the scrub section of the extractor contained essentially all tantalum and the extraction section all niobium. Thus a large amount of solute was recycled in both sections of the extractor. This was desirable since it was known that a large amount of solute recycling was necessary to obtain pure end products.

Since the tantalum product was not as pure as desired, it was evident that the amount of solute refluxing had to be increased, at least in the scrub section. It was decided to increase the solute recycle by adding more stages on that section of the column.

From the information gained on the first simulated column run the conditions for the second test were set as follows:

Feed: 35 milliliters of diethyl ketone feed solution added at stage seven.

Scrub: 140 milliliters of one molar sulfuric acid added at stage one.

Organic: 35 milliliters of diethyl ketone added at stage nine.

The column then consisted of seven scrub stages with O/A = 1/2 and two extraction stages with O/A = 1/4. Fifty cycles of this run were made, after which, the stages were analyzed. The results are presented in Table 11.

The data showed in this case that neither pure niobium nor tantalum was produced. Every tenth cycle product was analyzed and the results confirmed the stagewise data. It can be seen that the analysis of the organic phase in stage four indicated pure tantalum was present in this stage. This indicated that a small amount of niobium contamination was introduced with the scrub. However, a check of the scrub solution showed no niobium contamination present. It was concluded that either the analyses were in error or the one molar sulfuric acid concentration was too high

Table 11. Stagewise analyses for the second niobium-tantalum simulated column run using diethyl ketone

Stage number	Organic phase			Aqueous phase		
	Volume (ml)	Grams oxide/ liter	Per cent Ta_2O_5	Volume (ml)	Grams oxide/ liter	Per cent Nb_2O_5
1	24.5	57.01	99.98	74.2	12.59	0.04
2	27.9	79.38	99.94	73.0	19.61	0.02
3	30.0	94.43	99.97	74.8	24.61	0.03
4	29.0	104.9	>99.99	73.0	30.92	0.02
5	32.0	115.9	99.99	76.0	34.73	0.04
6	29.8	122.6	99.98	72.0	31.10	0.92
7	32.3	110.8	99.68	75.5	37.42	87.33
8	16.9	48.12	97.70	73.0	29.30	97.00
9	17.4	7.84	49.54	75.0	24.66	99.60

to effect a large amount of solute recycle. Since duplicate analyses were run and each checked within 10 per cent, it was decided to reduce the sulfuric acid concentration of the scrub.

Phase separation was slow when water and 0.05 molar hydrofluoric acid were used as scrub solutions. Adequate settling rates were found when 0.10 normal sulfuric acid was tried. In the first two runs noticeable volume changes occurred where fresh diethyl ketone and the sulfuric acid were added. Experiments were made with various mixtures of virgin

and equilibrated diethyl ketone and sulfuric acid. The system which gave the least organic volume change was chosen. This requirement was met by using virgin diethyl ketone and diethyl ketone equilibrated 0.10 normal sulfuric acid.

Two short simulated column runs were made to check the mass transfer and settling rates of the new system. Spectrographically-pure niobium and tantalum were produced in these runs. Since only 12 cycles of each of these two runs were made, stagewise samples were not taken because it was doubtful that steady state had been approached. However, the conditions of these two runs furnished enough information so that more specific conditions were set for the next test.

A fifth diethyl ketone simulated column run was made under the following conditions:

Feed: 50 milliliters of diethyl ketone feed solution added at stage four.

Scrub: 100 milliliters of diethyl ketone equilibrated 0.10 normal sulfuric acid added at stage one.

Organic: 50 milliliters of diethyl ketone added at stage seven.

The extraction process was carried out for 100 cycles, although only the products from every tenth cycle were analyzed. Analyses of the liquid phases in each stage were carried out after the extraction process was completed.

The cycle analyses indicated that about 40 cycles of operation were

Table 12. Stagewise analyses for the fifth niobium-tantalum simulated column run using diethyl ketone

Stage number	Organic phase			Aqueous phase		
	Volume (ml)	Grams oxide/ liter	Per cent Ta_2O_5	Volume (ml)	Grams oxide/ liter	Per cent Nb_2O_5
1	43.5	49.48	>99.99	52.0	29.36	0.013
2	43.3	80.43	>99.99	51.5	43.14	0.020
3	46.0	93.00	>99.99	55.0	42.01	3.33
4	46.0	90.83	99.44	55.5	68.29	87.00
5	27.0	40.62	90.38	56.0	54.93	96.55
6	24.0	12.22	39.97	54.0	52.40	99.74
7	26.2	5.21	4.09	54.0	51.54	>99.93

required to closely approach steady state. These analyses showed that the niobium delivered in the aqueous product contained less than 700 ppm tantalum. These data were substantiated by the stagewise data which appear in Table 12. It can be noted from the data in this table that the tantalum in the equilibrium organic phase of stages 1, 2 and 3 was spectrographically free of niobium. Since high purity tantalum was obtained in these three end stages it is probable that the contamination of the tantalum by niobium in the organic product phase was considerably less than 100 ppm, the lower limit of detection.

Analyses of the aqueous product phase indicated that the niobium in

this phase contained less than 700 ppm tantalum. Although this was the limit of detection for tantalum in niobium, it was estimated (46) that the niobium probably contained less than 300 ppm tantalum.

The equilibrium stagewise data were plotted in Figure 4. Compatible operating line data were found in the extraction section. The curvature of this line was explained by the volume changes noted in the data. The operating line for the first three stages of the scrub section defined a nearly straight line. However, the large amount of mass transfer which occurred near the feed stage undoubtedly caused volume changes which caused the operating line to curve a little. The position of the operating point between stage three and four could not be explained. The odd curvature of the equilibrium curve in the scrub section was probably the contributing factor for this effect.

Table 12 also revealed that the equilibrium aqueous concentration in stage three was less than the aqueous concentrations of stages two and four. It was apparent that something was being added in the feed which affected the scrub stage adjacent to the feed stage since this same effect can be noted in Tables 10 and 11.

The excess hydrofluoric acid was determined in each organic and aqueous equilibrium phase. The results are shown in Table 13. The total amount of fluoride was determined in each equilibrium phase. From the analyses the amount of fluoride required for H_2TaF_7 and H_2NbOF_5 was calculated. The excess hydrofluoric acid concentration was determined by difference. Some negative excess hydrofluoric acid values were found

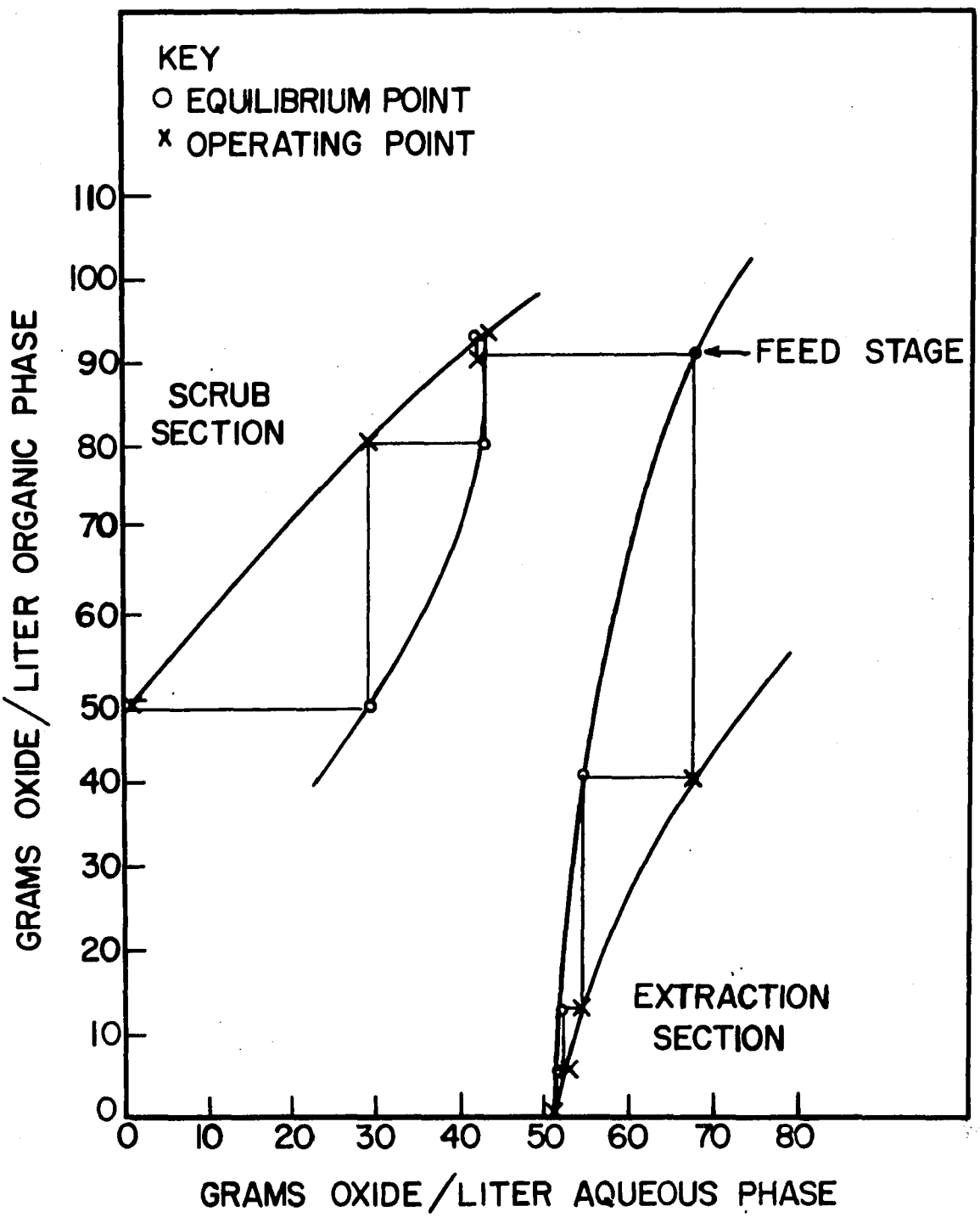


Figure 4. Equilibrium diagram for the fifth diethyl ketone simulated column run

Table 13. Stagewise excess hydrofluoric acid determination for the equilibrium phases of the fifth simulated column run using diethyl ketone

Stage number	Organic phase		Aqueous phase	
	Total HF (moles/l)	Excess HF (moles/l)	Total HF (moles/l)	Excess HF (moles/l)
1	1.403	-0.165	0.892	-0.038
2	2.131	-0.417	1.468	0.101
3	2.656	-0.292	1.773	0.433
4	3.275	0.394	4.461	1.945
5	2.090	0.912	4.197	2.142
6	1.362	0.941	3.851	1.881
7	1.016	0.821	3.170	1.231

in the scrub section of the extractor. This probably meant that some $HTaF_6$ was present in these streams. This effect, however, was determined to be helpful to the separation.

It was seen earlier in Figure 2 that $HTaF_6$ was not as extractable as H_2TaF_7. Hence, if some $HTaF_6$ were present in the extractor, it would prefer the aqueous phase and thus increase the recycle of solutes. The equilibrium distribution of hydrofluoric acid between diethyl ketone and 0.1 normal sulfuric acid was determined. The values from Table 13 plotted in a very irregular manner with this data indicating that niobium and tantalum

influenced the excess hydrofluoric acid equilibrium.

The excess hydrofluoric acid concentration increased rapidly between the equilibrium aqueous phases of stages three and four. It was probable then that the acid concentration affected the oxide concentration in these stages.

Simulated column runs using hexone

Hexone solutions containing various concentrations of niobium and tantalum oxides and excess hydrofluoric acid were used in these tests. The first simulated column run with hexone was a short test to check mass transfer and settling rates. The same flow rates that were used in the fifth diethyl ketone run were used in this and following tests. The aqueous scrub solution was 0.1 normal sulfuric acid equilibrated with hexone. The organic extraction solution was virgin hexone. The feed solution for this run was a hexone solution containing 292 grams oxide per liter and assaying 16.1 per cent tantalum oxide and 83.9 per cent niobium oxide. The excess hydrofluoric acid concentration was determined to be 4.4 normal. From this short test it appeared that hexone was identical to diethyl ketone as an extraction solvent as the mass transfer, settling rates, and end product purities were very similar.

In the second simulated column run with hexone an attempt was made to study the effect of composition on the separation. A portion of the above feed solution was diluted with hexone to yield a feed solution containing 209 grams oxide per liter and 3.15 normal in excess hydrofluoric acid

concentration.

The following conditions were followed for the second simulated column run using hexone:

Feed: 50 milliliters of hexone feed solution added at stage four.

Scrub: 100 milliliters of hexone equilibrated 0.10 normal sulfuric acid added at stage one.

Organic: 50 milliliters of diethyl ketone added at stage seven.

Thirty cycles of this run were made, the run was stopped, and the equilibrium stages analyzed. The results are presented in Table 14 and Figure 5.

Since the feed concentration, excess hydrofluoric acid concentration, and extraction conditions were similar for the second hexone run and the fifth diethyl ketone run, comparison of the data from these runs indicated the effect of feed composition on the extraction. This comparison was true if the diethyl ketone and hexone were assumed to have equal extraction power for this system. A comparison of the equilibrium stagewise composition showed diethyl ketone a slightly better extracting agent than hexone. However, since product purities were apparently identical, it was difficult to attach a significant difference between the extracting power of these two ketones on this particular system.

The effect of composition on the extraction was clearly seen by comparing Figures 4 and 5. Increasing the niobium content of the feed solution caused both equilibrium curves to shift. Since identical flow

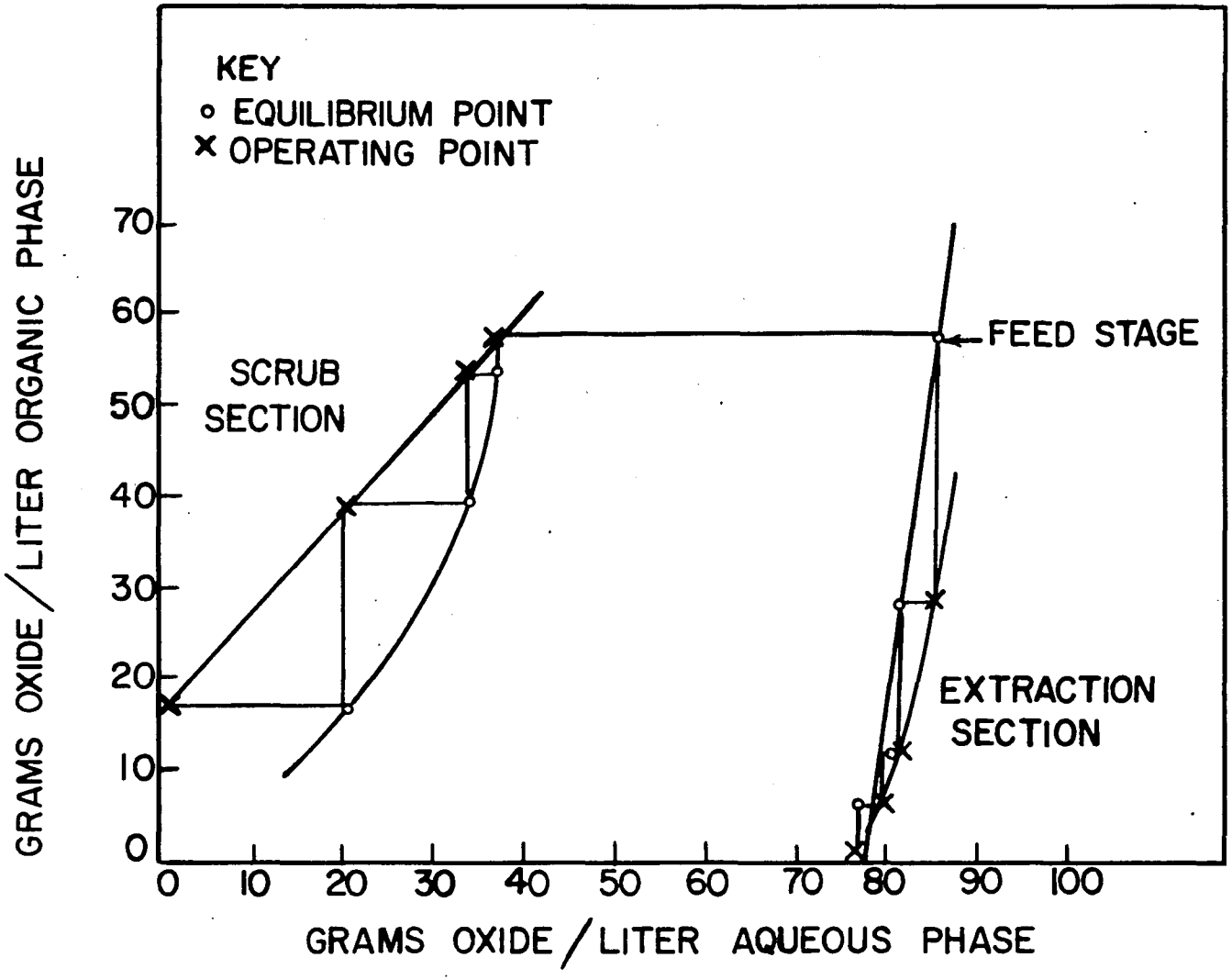


Figure 5. Equilibrium diagram for the second hexone simulated column run

Table 14. Stagewise analyses for the second niobium-tantalum simulated column run using hexone

Stage number	Organic phase			Aqueous phase		
	Volume (ml)	Grams oxide/ liter	Per cent Ta_2O_5	Volume (ml)	Grams oxide/ liter	Per cent Nb_2O_5
1	43.8	16.88	>99.99	51.0	20.39	0.050
2	46.0	39.14	>99.99	52.0	33.92	0.044
3	45.5	53.69	>99.99	53.3	36.83	7.43
4	45.0	57.44	97.57	58.0	85.43	84.37
5	25.5	28.64	82.65	56.0	81.59	97.67
6	25.0	11.50	48.65	53.0	80.79	99.45
7	26.0	6.09	5.00	54.0	76.92	>99.93

rates were used in both runs, the extraction equilibrium curve shifted to the right because of the increased niobium content in the aqueous phases. Similarly the equilibrium curve for the scrub section shifted to the left because of the decreased tantalum content in the scrub equilibrium aqueous phases. Both equilibrium curves were shifted downward because of the decreased tantalum content in the equilibrium organic phases.

It can also be seen by a comparison of Figures 4 and 5 that the operating and equilibrium curves for the scrub section of the two extraction runs were quite similar. On the other hand, the operating and equilibrium

curves for the extraction section were different. The operating curves in both scrub sections were very nearly straight lines. This indicated that volume changes in this part of the extractor were virtually non-existent. The curvature of the extraction operating curve for the diethyl ketone run indicated high diethyl ketone solubility in the sulfuric acid aqueous phase whereas the curvature of the corresponding curve for the hexone run indicated an increase in the organic phase with a decrease in the aqueous phase. These conclusions were verified by the data in Tables 12 and 14. It was unlikely, however, that the sulfuric acid aqueous phases in the hexone run were soluble in the organic phases to the extent shown by the curvature of the extraction operating line in Figure 5. It was more probable that the mass transfer between phases caused the volume changes. Since virgin hexone and diethyl ketone were fed in these experiments, some volume change was expected because of solubility. The mass transfer which occurred between stages, then, apparently overshadowed the solubility of hexone in the acid phases resulting in increased organic volumes. For diethyl ketone the mass transfer between stages was not great enough to counteract the solubility and decreased organic volumes resulted. For economical reasons hexone was preferred as the extracting agent over diethyl ketone because of the higher solvent recovery value and lower initial cost.

A third simulated column run using hexone was made to study the effect of higher feed concentrations on the extraction. The feed solution previously used in hexone simulated column run number one was run in this experiment. The conditions of the run were as follows:

Feed: 50 milliliters of hexone feed solution added at stage four.

Scrub: 100 milliliters of hexone equilibrated 0.10 normal sulfuric acid added at stage one.

Organic: 50 milliliters of hexone added at stage seven.

Eighty-one products were taken off this run with the products from every tenth cycle analyzed. Analyses of the liquid phases in each stage were carried out after the extraction process was completed.

The cycle analyses indicated that less than 20 cycles of operation were required to closely approach steady state. These analyses showed that the tantalum delivered in the organic extract contained less than 100 ppm niobium. The niobium raffinate was assayed and showed less than 700 ppm tantalum present. These data were confirmed by the stagewise data which appear in Table 15.

For comparative purposes the stagewise data were plotted in Figure 6. As expected the higher concentration in the feed solution shifted the equilibrium curves. It was also noted that the reversal effects present in the diethyl ketone runs of the scrub stage adjacent to the feed stage were absent. Apparently the excess hydrofluoric acid distribution between equilibrium phases was not as drastic as had been found in the diethyl ketone runs.

The effect of feeding virgin hexone into the extractor was evident in Figure 6. Employing sulfuric acid equilibrated hexone in place of virgin hexone would probably remedy this situation and decrease the curvature of

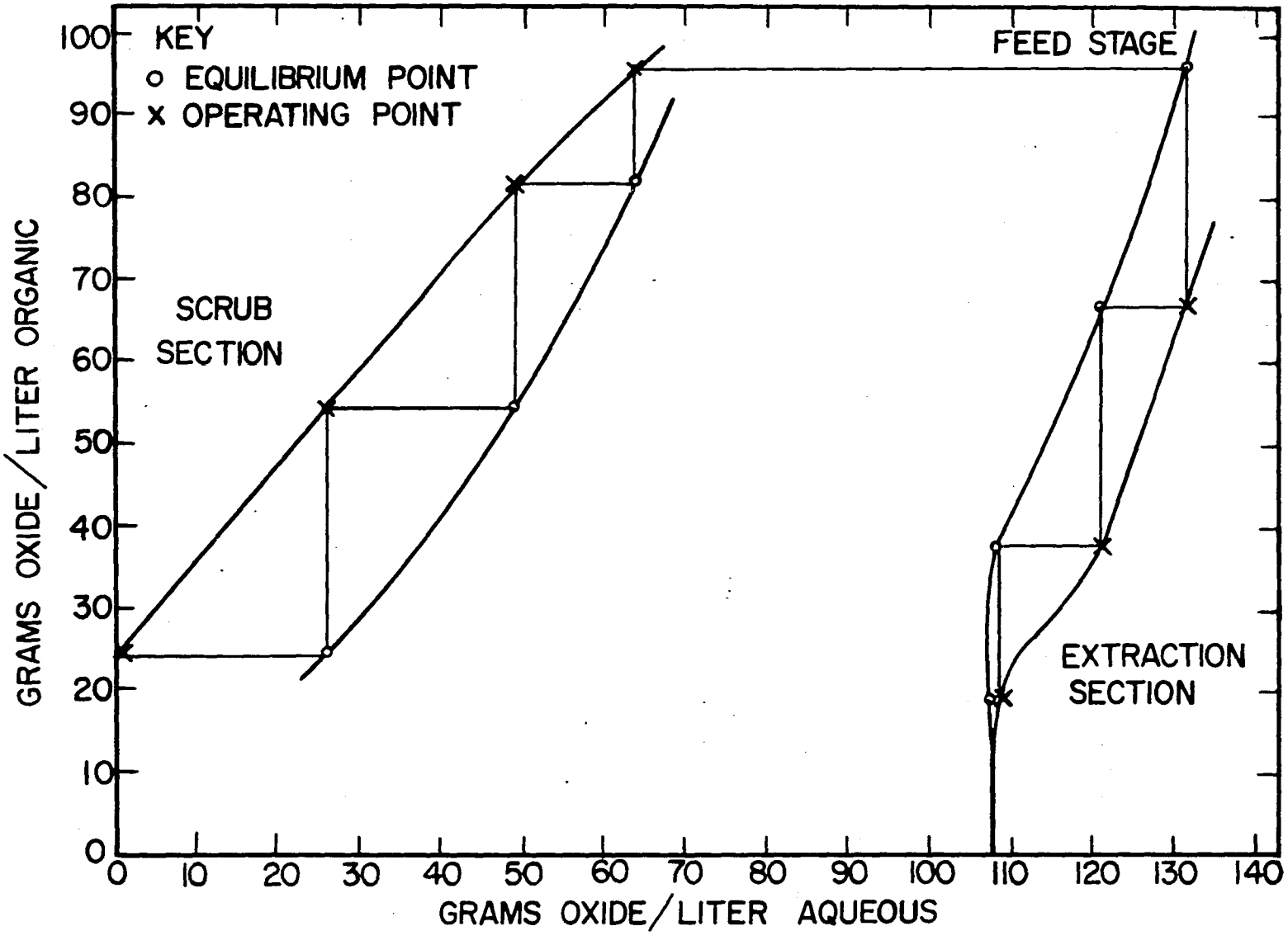


Figure 6. Equilibrium diagram for the third hexone simulated column run

Table 15. Stagewise analyses for the third niobium-tantalum simulated column run using hexone

Stage number	Organic phase			Aqueous phase		
	Volume (ml)	Grams oxide/ liter	Per cent Ta_2O_5	Volume (ml)	Grams oxide/ liter	Per cent Nb_2O_5
1	38.0	24.08	>99.99	51.5	26.23	0.029
2	40.3	54.39	99.985	52.5	49.09	0.135
3	42.0	81.35	99.980	54.0	63.81	8.38
4	45.5	95.85	94.41	56.0	131.43	79.02
5	26.0	66.48	86.17	55.0	121.03	90.57
6	26.5	37.35	61.61	58.5	108.67	98.25
7	26.3	18.48	24.49	56.5	107.13	>99.93

the operating line.

It was desired to test the separation process as predicted by the preceding simulated column runs in a pilot plant extractor. Two large batches of hexone feed solution were prepared in the following manner. The Nigerian ore concentrate reported in Table 3 was the source material for the niobium and tantalum.

One hundred and twenty-five pounds of this ore were mixed with cold hydrofluoric acid in two polyethylene carboys, one 75 pound batch and one 50 pound batch. The reactants were shaken together for approximately one

month. At the end of this period hexone was added and the solutions were filtered through saran cloth into a polyethylene carboy. Approximately one-half of the ore was found unreacted in the fluoride cake.

Since the reaction was only 50 per cent effective the hexone feed solution contained a large excess of hydrofluoric acid. Excess acid was undesirable because from the data of Figure 2 it was predicted that separation would be relatively poor. In addition, extraction employing this high acid feed solution was not a fair test for the process under consideration. It was hoped to follow the conditions set forth earlier for the preparation of the extractor feed solution. This was not always possible because of the lack of suitable equipment in the laboratory.

It was found that a one stage extraction employing one volume of concentrated sulfuric acid to 10-15 volumes of the high acid hexone feed solution was suitable for removing most of the hydrofluoric acid. This extraction also served to remove iron, manganese, and some niobium from the feed solution. In fact the oxide concentration of the feed solution increased during this extraction. A volume reduction of approximately 10 per cent was also noted for the hexone solution.

Approximately 15 gallons of hexone feed solution were obtained by this method. The solution contained 305 grams oxide per liter assaying 14.0 per cent tantalum oxide and 86.0 per cent niobium oxide. The excess hydrofluoric acid concentration was determined as 5.4 normal. The feed solution should have assayed 9.0 per cent tantalum oxide and 91.0 per cent niobium oxide had the opening of the ore been complete. However, some

niobium was lost when the feed solution was contacted with concentrated sulfuric acid. More loss occurred during the leaching process. Due to lack of suitable equipment, the leaching was not complete. Since tantalum extracted first, that which was left in the cake was mostly niobium.

A 16 stage polyethylene, mixer-settler extractor, developed at this laboratory, was available. At first it was decided to use 13 of these stages in the test. In order to properly set the interface controls on the extractor, stagewise density data were necessary. A 13 stage simulated column run was started to obtain this information. The following conditions were followed:

Feed: 50 milliliters of hexone feed solution added at stage seven.

Scrub: 100 milliliters of hexone equilibrated 0.10 normal sulfuric acid added at stage one.

Organic: 50 milliliters of hexone added at stage thirteen.

After 15 cycles of operation were completed, the concentration of the product streams was tested. The tantalum extract was found to contain only six grams oxide per liter. It was decided to reduce the total number of stages to nine so that a more concentrated product could be realized.

Rather than start a nine stage simulated column run it was decided to eliminate stages 1, 2, 12, and 13 of the run already in progress. The feed stage was now stage five. Ten more products were collected and the extractor sampled stagewise. This data along with the density data are presented in Table 16. Equilibrium and operating curves are shown in

Table 16. Stagewise analyses for the fourth niobium-tantalum simulated column run using hexone

Stage number	Organic phase			Density grams/ml	Aqueous phase			Density grams/ml
	Volume (ml)	Grams oxide/liter	Per cent Ta_2O_5		Volume (ml)	Grams oxide/liter	Per cent Nb_2O_5	
1	36.3	20.21	>99.99	0.829	49.0	24.08	0.023	1.027
2	37.0	46.84	>99.99	0.867	54.0	47.67	0.025	1.050
3	39.5	78.14	>99.99	0.907	51.8	72.22	0.033	1.077
4	43.0	106.1	>99.99	0.944	58.5	91.50	4.95	1.103
5	46.5	128.2	99.72	0.980	59.5	161.9	67.66	1.201
6	28.0	119.4	95.84	0.971	62.5	154.8	73.61	1.188
7	29.0	94.48	91.73	0.941	58.0	141.4	80.82	1.176
8	28.0	64.47	80.05	0.907	61.0	136.1	90.99	1.157
9	27.5	31.74	55.31	0.862	55.0	111.3	98.85	1.148

Figure 7.

The aqueous product from stage nine assayed 1.15 per cent tantalum oxide in niobium oxide indicating that steady state had not been reached. The main purpose of the simulated column run was to obtain the density relations of the equilibrium phases. For the purpose intended, these data were suitable. However, it was also desired to obtain good equilibrium data so that a comparison between the predicted equilibrium and the actual equilibrium in the continuous extractor could be made. It was probable that the steady state equilibrium conditions were close enough to the data in Table 16 so that a rerun of the simulated column was not warranted.

Continuous countercurrent extraction run

A 16 stage polyethylene, mixer-settler type extractor (47) was employed for the continuous extraction run. Since this extractor was still under development, this run also served to test the operational characteristics of the extractor. Only ten stages of the extractor were actually used, nine stages for the extraction and the tenth stage as a raffinate overflow. Figure 8 is a photograph of the extractor.

The continuous extraction run was carried out for eleven hours. The hexone feed solution was added at stage five at a rate of 44 milliliters per minute. Aqueous scrub was added at stage one and virgin hexone was added at stage nine at a rate of 88 and 44 milliliters per minute respectively. No difficulty was encountered with the interface control

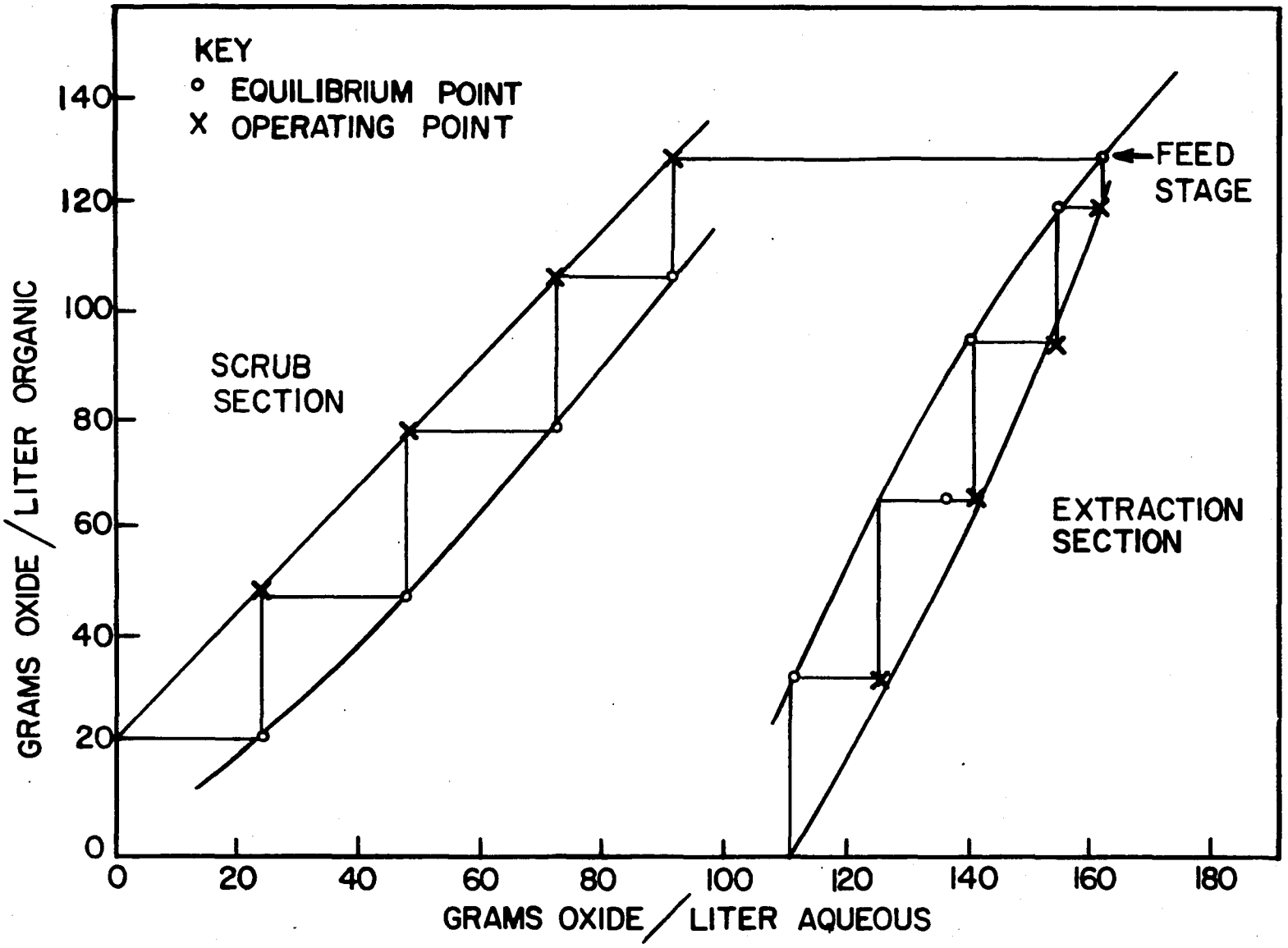


Figure 7. Equilibrium diagram for the fourth hexone simulated column run

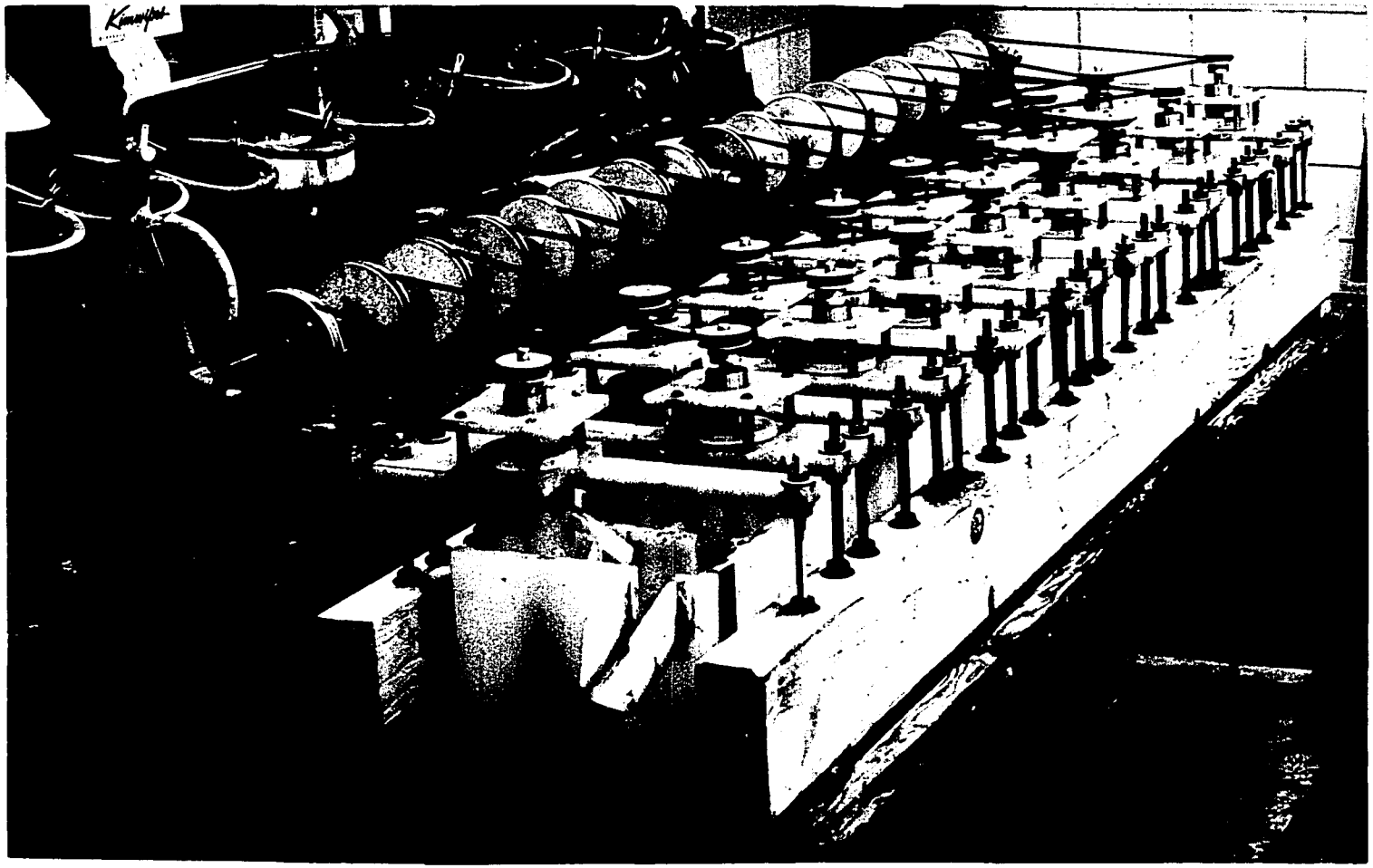


Figure 8. Photograph of the polyethylene mixer-settler extractor

or settling of phases during the run. Attempts to run at higher flow rates caused settling difficulties in stages eight and nine. However, this difficulty was attributed to the extractor and not the system as the capacity of the extractor was probably being exceeded.

Before the liquid hold up in the extractor was displaced once, i.e., before one through-put, tantalum containing less than 100 ppm niobium was being produced in the extract product. After approximately two through-puts, the raffinate product contained niobium with less than 700 ppm tantalum. The difference in the time element before the pure products were noted was probably due to some contamination of the extraction solution while the flow rates were being adjusted. Higher flow rates than those finally settled upon were first attempted. The emulsion that formed in stages eight and nine caused some organic solution from the scrub section to back up into the extraction section which undoubtedly caused higher tantalum concentrations than ordinarily present.

At the end of the extraction run the equilibrium phases were removed from the extractor and assayed. The data obtained are presented in Table 17. It was apparent from these data that the actual equilibrium concentrations did not correspond to the predicted values. Periodic checks of the flow rates were made during the course of the run. For the first 10 hours the flow rates were essentially the same as those set at the start. However, the last check, made just before the run was stopped, showed that the feed rate had decreased to 25 milliliters per minute. During the last hour then, this flow rate changed drastically enough to affect the

Table 17. Stagewise analyses for niobium-tantalum continuous extraction run

Stage number	Organic phase		Aqueous phase	
	Grams oxide per liter	Per cent Ta_2O_5	Grams oxide per liter	Per cent Nb_2O_5
1	25.35	>99.99	14.15	0.12
2	39.65	>99.99	14.18	3.20
3	40.73	99.97	11.27	44.69
4	34.34	96.70	35.17	86.30
5	60.12	47.03	125.9	96.70
6	53.33	19.79	130.8	99.02
7	49.80	7.35	132.1	99.61
8	48.20	1.80	132.7	99.86
9	39.80	0.82	125.9	>99.93

equilibrium of the extractor. Since the time necessary for one throughput was a little more than one hour, the change was still occurring when the extractor was stopped. The data in Table 17 confirmed this observation.

The raffinate and extract product containers were changed periodically during the course of the run. These data confirmed that the extractor apparently operated close to the predicted equilibrium as shown by the raffinate and extract concentrations. For the first ten hours of the run

the extract and raffinate streams averaged 22 and 108 grams oxide per liter respectively.

The sulfuric acid raffinate from the first extractor contained the niobium and the minor impurities present. In order to produce reactor-grade niobium oxide, it was desired to separate the niobium and the minor impurities by a second extraction. Tests employing the simulated column technique showed that both a large volumetric flow rate of organic to aqueous and a large number of stages were necessary.

However, when a continuous extraction was made employing 15 stages, a volumetric flow ratio of organic to aqueous of four to one was found to extract about 95 per cent of the niobium in the original feed. Since it was impossible to increase this flow ratio without exceeding the capacity of the extractor, a volumetric flow ratio of organic to aqueous of ten to one was chosen for the purposes of the cost analysis. This value may be somewhat high but it provided a safety factor for the final cost estimate.

Solvent Treatment and Recovery

Under normal conditions for a process employing a solvent separation process the extracted solute is stripped from the solvent by an aqueous solution. In most cases this stripping operation is sufficient to remove essentially all the solute and produce a solvent acceptable for reuse by direct recycle. For the case of tantalum and niobium in hexone, however, this method of operation was not acceptable. Such large volumes of aqueous solution were necessary to strip the solute that hexone losses were high

because of solubility. In addition the number of stages required exceeded the number necessary for the initial separation.

Solvent recovery by stripping of the solute

Various aqueous solutions were tested in an attempt to find a suitable stripping agent. Among the solutions tested were: distilled water, concentrated sulfuric acid, 0.05, 0.10, 0.25, 1.0, 2.0, 6.0 and 12.0 normal sulfuric acid, 0.05, 0.10, 0.25, and 0.50 normal hydrofluoric acid, 0.05, 0.10, 0.25, 0.50, 1.0 and 2.0 normal ammonium bifluoride solutions, ammonium nitrate, sulfate, and chloride solutions, dilute mixtures of sulfuric and hydrofluoric acids, and a mixture of 2 normal ammonium bifluoride and one normal sulfuric acid. This last mixture along with the dilute sulfuric acid solutions appeared to be the most promising solutions. However, in no case was the hexone found to be free of solute after the stripping operations.

Flow rate ratios of strip solution to hexone as high as ten to one were employed in as many as nine stages. Under these extreme conditions very little hexone solution was usually produced as the solubility was quite high. With flow rate ratios of two, three, and five to one, appreciable solute was usually still found in the hexone.

Solvent recovery by precipitation of the solute

Precipitation of the solute in the hexone by the addition of ammonium hydroxide was found to be the most desirable method tested for solute removal. A slight excess of ammonium hydroxide over that required to

precipitate the solute was added directly to the hexone. The precipitate was allowed to settle and the solution filtered. A two phase filtrate resulted with about 7 per cent by volume being an aqueous phase. The two phases were separated and the aqueous solution discarded. The hexone was regenerated by equilibrating with a small volume of dilute sulfuric acid. Ninety-two per cent of the hexone was recovered in this manner. Acid requirements were determined as 0.012 pounds sulfuric acid per pound of hexone regenerated.

The scale at which these extractions were made did not allow for extensive tests on solvent recycling or degradation. Single stage shake up tests were made to compare the extracting power of virgin and regenerated hexone. The regenerated hexone was the better extraction agent in every case. In addition, volume changes were less severe. It was concluded that equilibrated hexone should be used for all the extractions and that regenerated hexone was suitable for reuse provided it was regenerated under the above conditions.

Solvent losses

The losses of solvent in the extraction process were quite small and therefore difficult to measure. Hexone losses by evaporation were undoubtedly present. However, if a closed extractor were employed, evaporation losses would be negligible. The principal sources of loss for hexone were probably solubility in the aqueous phase, entrainment by the leaving raffinate, and the eight per cent loss in the solute stripping

operation. The reported solubility of hexone in water was 19.0 grams per liter, but it was found that solubility in acid was less than in distilled water. For the purposes of the cost estimate, the overall solvent loss was estimated at 10 per cent of the initial amount required for the extraction.

Final Conversion of Products

General requirements

The purified niobium and tantalum fractions were converted to the hydroxides in the solvent recovery scheme. Separation of the hydroxides from the solvent was effected by filtration. It was necessary to wash, dry, and calcine the hydroxides to tantalum and niobium oxides. For the purposes of this proposed process the purified oxides were assumed suitable for reduction to their respective metals. If other salts proved more useful for metal reduction, they could be obtained by a simple modification in the process or by direct conversion of the oxides.

The wet hydroxides contained 3.5 pounds of water per pound of solids. Filter requirements, computed for a plate and frame pressure filter, were 0.33 square feed per pound of oxide produced. Ammonia requirements were 1.11 pounds of 100 per cent ammonia per pound of tantalum oxide and 1.32 pounds per pound of niobium oxide. The yields were essentially 100 per cent. Wash water amounted to roughly one gallon per pound of oxide. The washed cakes were dried and calcined at about 500° C. to produce niobium and tantalum oxides.

Product purities

The niobium and tantalum oxides produced by this method were spectrographically pure with respect to each other. Trace impurities were determined by emmission spectrograph. In all cases these trace impurities amounted to only a trace of iron and a faint trace of manganese. Quantitatively, then, these impurities probably amounted to less than 50 ppm.

COST ANALYSIS

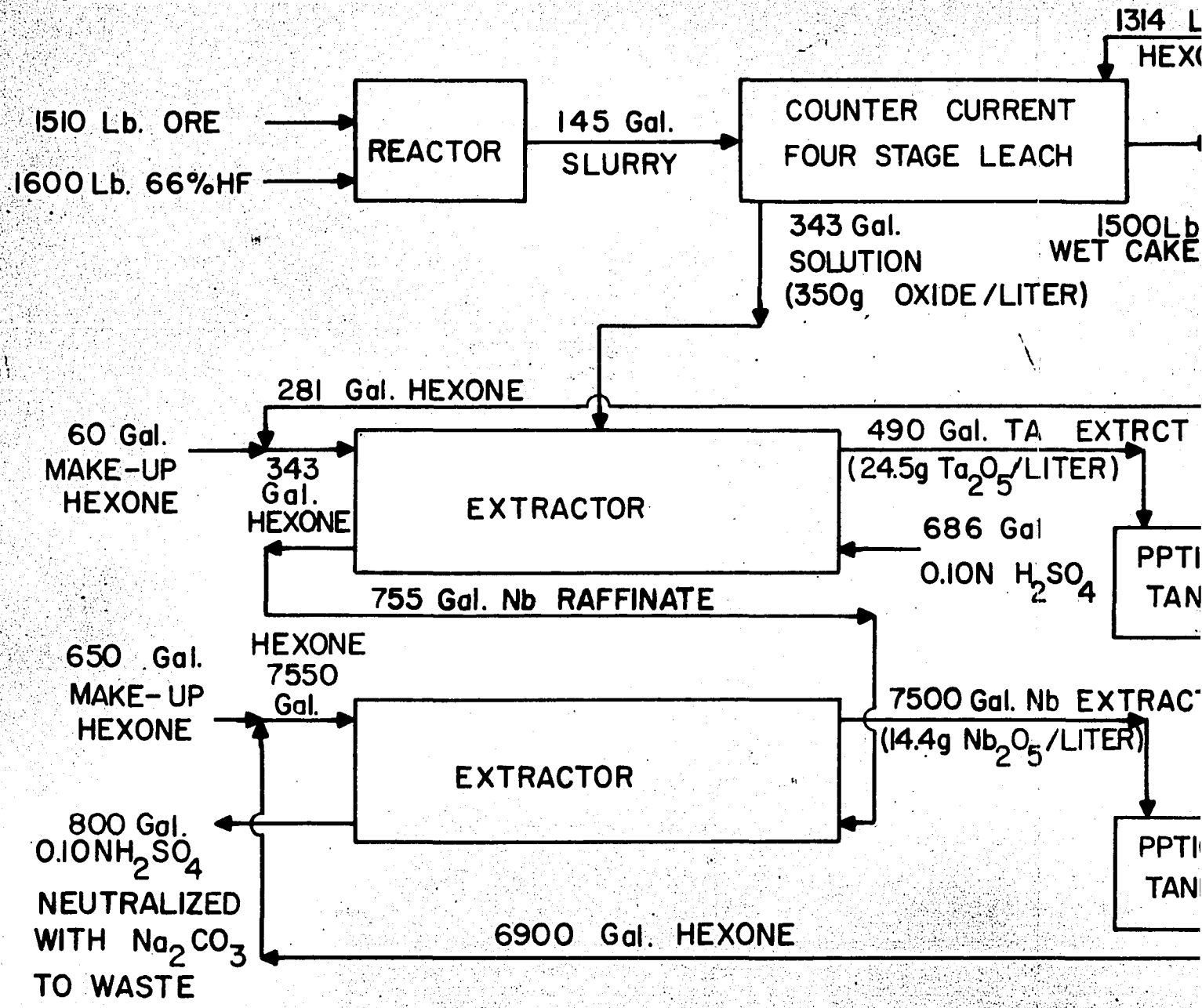
A cost analysis for production of tantalum-free niobium and niobium-free tantalum was made from the information and experience obtained in the investigation. No detailed plant design calculations were carried out. Plant location was chosen as the Niagara Falls, New York area as a basis for freight and other dependent charges because of its favorable utility resources. The raw material basis was an ore concentrate containing 70 per cent total oxides and assaying 63 per cent niobium oxide and 7 per cent tantalum oxide.

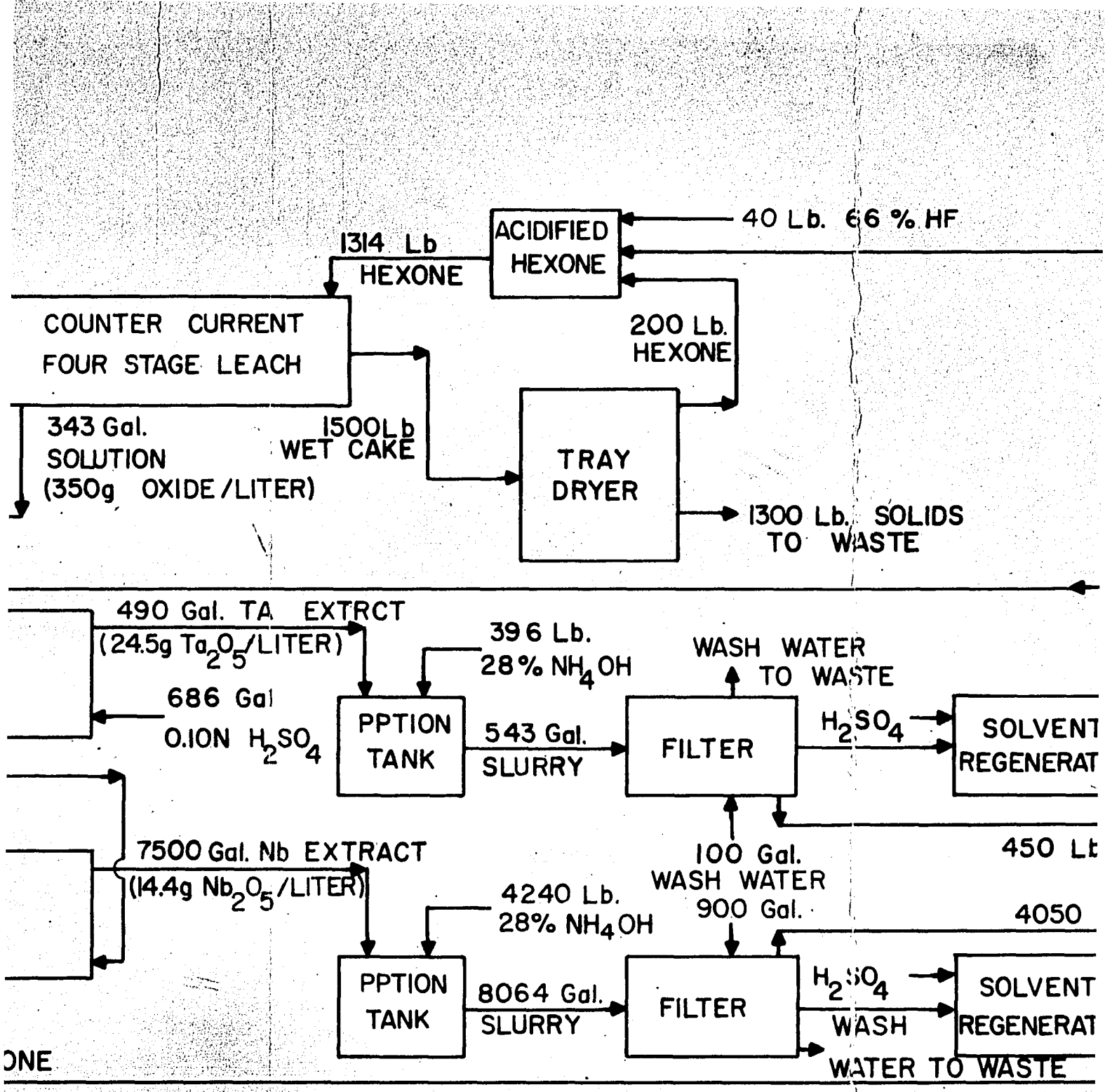
The daily production rate for the purification plant was chosen as 1000 pounds of total oxide (equivalent to 900 pounds Nb_2O_5 and 100 pounds Ta_2O_5) per day based on operation for an average of 300 days per year. While in operation the plant would run for 24 hours per day and six days per week. This size of plant roughly approximates the several zirconium plants which have been recently constructed. This basis permitted one to compare niobium directly with zirconium, the one metal with which niobium necessarily must compete for many of the proposed uses.

The raw materials and equipment costs were made for the process following the flow sheet in Figure 9. This flow sheet is a summary of the recommended conditions given for previous steps of the process.

Figure 9. Quantitative flow diagram for the proposed process

BASIS: ONE DAY OPERATION

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1314 Lb HEXONE
COUNTER CURRENT FOUR STAGE LEACH
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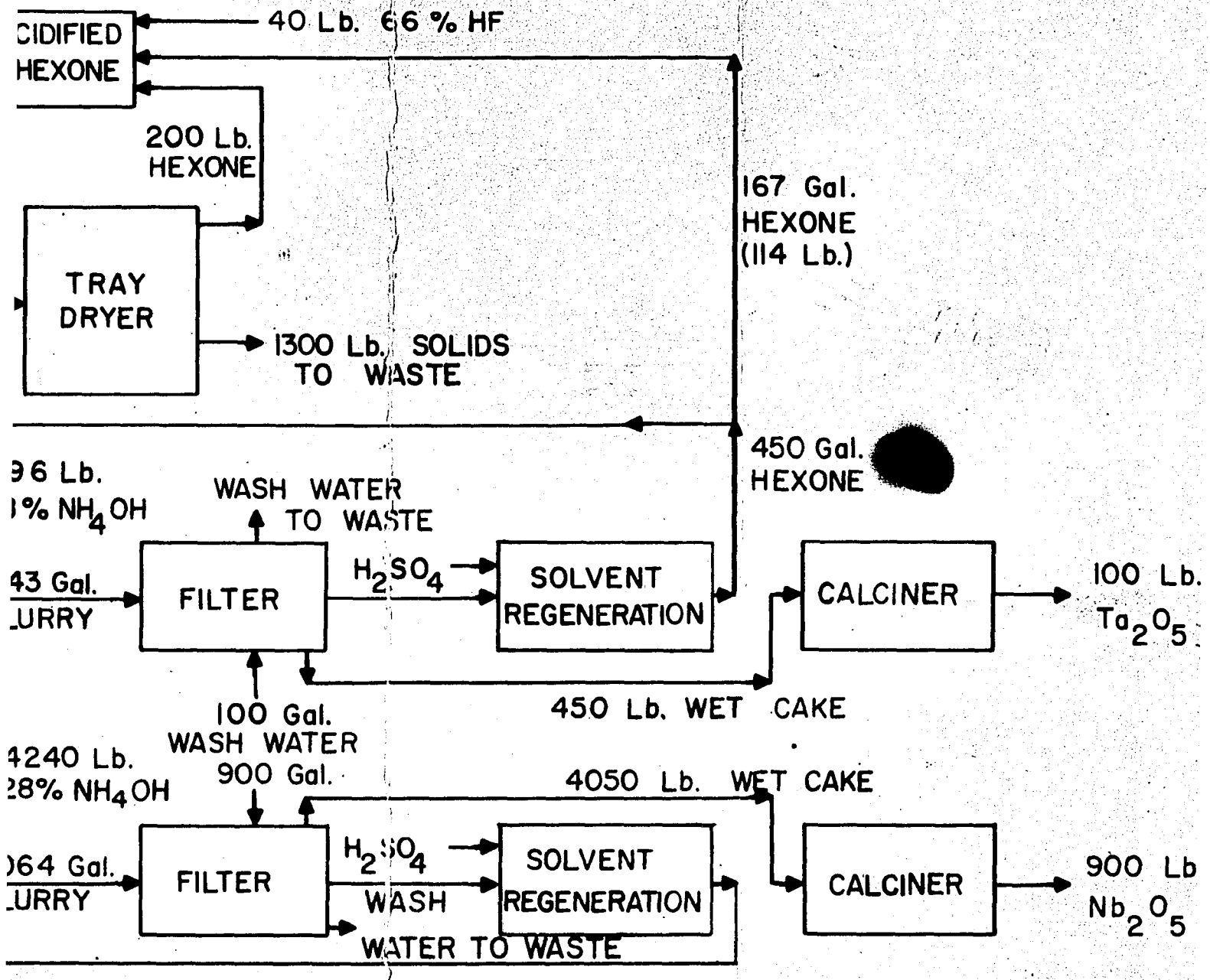
1500 Lb WET CAKE
TRAY DRYER
1300 Lb. SOLIDS TO WASTE
490 Gal. TA EXTRCT (24.5g Ta_2O_5/LITER)
396 Lb. 28% NH_4OH
WASH WATER TO WASTE
686 Gal 0.10N H_2SO_4
PPTION TANK
543 Gal. SLURRY
FILTER
H_2SO_4
SOLVENT REGENERAT
450 Lb
7500 Gal. Nb EXTRACT (14.4g Nb_2O_5/LITER)
100 Gal. WASH WATER
900 Gal.
4240 Lb. 28% NH_4OH
4050
PPTION TANK
8064 Gal. SLURRY
FILTER
H_2SO_4
WASH WATER TO WASTE
SOLVENT REGENERAT
ONE


CIDIFIED
HEXONE
40 Lb. 66 % HF
200 Lb.
HEXONE
TRAY
DRYER
1300 Lb. SOLIDS
TO WASTE
167 Gal.
HEXONE
(114 Lb.)
450 Gal.
HEXONE
96 Lb.
% NH_4OH
WASH WATER
TO WASTE
43 Gal.
URRY
FILTER
H_2SO_4
SOLVENT
REGENERATION
CALCINER
100 Lb.
Ta_2O_5
100 Gal.
WASH WATER
450 Lb. WET CAKE
4240 Lb.
28% NH_4OH
900 Gal.
4050 Lb. WET CAKE
064 Gal.
URRY
FILTER
H_2SO_4
WASH
WATER TO WASTE
SOLVENT
REGENERATION
CALCINER
900 Lb
Nb_2O_5

Chemical Costs

The raw materials required in processing were the major contribution to the cost of the finished product and were probably the most accurately known portion of the estimate. The cost of the columbite ore concentrate was taken from the latest quotation of the David Taylor Export Company (48). The costs of the other chemicals were estimated from listings in Chemical and Engineering News.

The basis of the chemical requirements was taken as one pound of oxide product or 0.90 pound niobium oxide and 0.10 pound tantalum oxide. Yields of niobium and tantalum were 100 per cent for all the processing steps except the hexone leaching step where the yield was taken as 95 per cent. Raw material costs are summarized in Table 18.

Equipment Costs and Investment

An estimate was made of the equipment required to process 900 pounds of niobium oxide and 100 pounds of tantalum oxide per day. The size of the equipment chosen was based upon data obtained in the laboratory and was taken only for the purpose of preliminary cost estimation rather than design. In most instances the costs were estimated from published data in Chemical Engineering Costs Quarterly and other sources (49-51). All estimated costs were based on November, 1956 by the use of the Marshall and Stevens all-industry index (51). A factor of 1.43 was used to determine the installed cost from the cost, F.O.B. the factory (52). The major equipment required for production of 900 pounds niobium oxide and 100

Table 18. Preliminary raw material cost estimate for the proposed niobium and tantalum purification process

Basis: one pound of oxide product (0.90 pound Nb_2O_5, 0.10 pound Ta_2O_5)

Chemical	Units/lb. product	Unit cost	Cost/lb. product
Ore concentrate 70 per cent oxide basis	1.51 lb.	$1.40/lb. contained oxides	$1.474
Hydrofluoric acid 66 per cent basis	1.64 lb.	0.1375/lb.	0.226
Methyl isobutyl ketone	1.04 lb.	0.13/lb.	0.135
Sulfuric acid 95 per cent basis	0.029 lb.	0.0112/lb.	0.001
Ammonia 100 per cent basis	1.296 lb.	0.0415/lb.	0.054
Soda ash 58 per cent basis	0.054 lb.	0.0115/lb.	0.001
Process water	2.0 gal.	0.35/1000 gal.	0.001
	Total for one pound of Nb_2O_5 or Ta_2O_5		$1.892

pounds of tantalum oxide per day are itemized in Table 19.

In calculating the total capital investment, the installed process equipment cost was used as the basis, with the investment for piping, instrumentation, and building estimated as a fraction of this cost. The procedure outlined by Zimmerman and Lavine (49) was used. Since it was considered that services such as steam and power would be purchased from outside sources, no estimates were included in fixed capital for these facilities. The distribution of capital investment is shown in Table 20.

Operating Costs

The raw material costs for the process have been estimated. The total operating charges include these costs plus those for utilities, labor, depreciation, maintenance, and administration. Labor requirements were estimated from experience in processing and handbook data upon labor needed for equipment operation. Hourly rates were based upon available data. Five operators and one foreman would be required per eight hour shift. The labor was distributed as follows:

Opening of the ore and feed preparation	2 operators/shift
Extraction	1 operator/shift
Oxide conversion and solvent recovery	2 operators/shift
Supervision	1 foreman/shift

The requirements for maintenance personnel, analysts, and office help

Table 19. Installed process equipment cost for the proposed niobium and tantalum purification plant

Basis: 1000 pounds oxide/day (900 pounds Nb_2O_5 and 100 pounds Ta_2O_5)

Number	Equipment	Total cost
1	Bin, 1000 ft.^{3}, wood	$ 1,500
1	Dryer, vacuum shelf, 20 ft.^{2} shelf area, monel clad	5,000
1	Extractor, mixer-settler type, closed, 9 stage, 1.5 gpm, polyethylene	7,500
1	Extractor, mixer-settler type, closed, 15 stage, 2.0 gpm, polyethylene	10,000
1	Filter, plate and frame, 12 inch, 12 chamber, one inch frames, cast iron	800
1	Filter, plate and frame, 36 inch, 40 chamber, one inch frames, open discharge, cast iron	4,400
1	Filter, rotary, horizontal, vacuum, closed, 27 ft.^{2}, wash accessories included, monel	43,000
1	Furnace, electric, 15 lb. H_2O/hr.	2,000
2	Furnace, electric, 70 lb. H_2O/hr.	3,000
1	Grinder, hammer mill, 1000 lb./hr.	1,400
20	Motor, one-half horsepower	1,000
20	Pump, centrifugal, 3.0 gpm, monel	6,000
3	Pump, slurry, 5.0 gpm, monel	2,500
2	Reactor, 50 gal., agitated, closed, steam coils, haveg	2,600

Table 19. Continued

Number	Equipment	Total cost
4	Tank, 50 gal., agitated, closed, haveg	$ 4,400
1	Tank, 100 gal., agitated, closed, haveg	1,300
1	Tank, 100 gal., closed, haveg	1,000
1	Tank, 500 gal., closed, haveg	1,400
2	Tank, 1000 gal., closed, haveg	4,000
1	Tank, 5000 gal., closed, steel	4,900
	Miscellaneous	20,000
	Total installed equipment costs	$127,700

were calculated as functions of installed equipment or labor costs.

The total capital investment was depreciated over a five year period. Power and steam requirements were not well known, but were estimated as 200 kilowatts and 100 pounds steam respectively. The procedure of Dybdal (53) was used in preparing the estimate. Direct and indirect conversion costs were estimated. The bulk manufacturing cost was the sum of the direct conversion cost, the indirect conversion cost, and the raw material cost. These items are presented in Table 21.

The process costs given are those for niobium and tantalum oxides rather than the metal. To these costs must be added the expense of

Table 20. Capital investment for the proposed niobium and tantalum purification plant

Basis: 1000 pounds oxides/day (900 pounds Nb_2O_5 and 100 pounds Ta_2O_5)

Subject	Cost
Installed process equipment (I.P.E.)	$127,700
Piping — 25 per cent of I.P.E.	31,900
Instrumentation — 10 per cent of I.P.E.	12,800
Building — 20 per cent of I.P.E.	25,500
Total plant cost (T.P.C.)	$197,900
Engineering and construction — 25 per cent of T.P.C.	49,500
Contingencies — 15 per cent of T.P.C.	29,700
Total capital investment	$277,100

Table 21. Preliminary process cost estimate for niobium-tantalum purification plant

Plant capacity: 1000 pounds oxide/day (900 pounds Nb_2O_5 and 100 pounds Ta_2O_5)

Basis: one pound of oxide product

	Unit cost	Cost
Direct conversion cost		
Labor, 0.12 man hours	$2.00/hr.	$0.240
Supervision, 0.024 man hours	3.00/hr.	0.072
Power, 4.8 KWH	0.01/KWH	0.048
Steam, 100 lb.	0.50/1000 lb.	0.050
Maintenance (10 per cent/year installed equipment)		0.042
Supplies (0.5 per cent/year installed equipment)		0.002
Laboratory		0.050
Payroll charges (15 per cent of labor and supervision)		0.047
Total direct conversion cost		$0.551
Indirect conversion cost		
Overhead (40 per cent of labor, supervision, and maintenance)		$0.142
Depreciation (20 per cent/year capital investment)		0.185
Taxes (2 per cent/year capital investment)		0.019
Insurance (1 per cent/year capital investment)		0.010
Total indirect conversion cost		$0.356
Raw materials		$1.892
Bulk manufacturing cost		$2.799

reduction to the metal in order to gain a concept of the relative importance of the proposed separation process. However, these costs are not generally available. If a metal reduction cost of 10 or even 20 dollars a pound is estimated, it is evident that the cost of these metals would be drastically reduced from their present price level. On this basis, then, this proposed process for the separation and purification of niobium and tantalum oxides could successfully compete with the processes presently employed.

DISCUSSION OF RESULTS

This investigation of the separation and purification of niobium and tantalum by hexone extraction was not complete enough to permit a detailed plant design. The primary objective was the determination of a preliminary cost estimate based upon data obtained in laboratory and pilot plant studies. However, the process itself has been fixed in its broad outlines and it is probable that very little further work will be required upon the qualitative flow sheet. Data for the sizing and exact operation of several pieces of equipment were not adequate. The problems yet unsolved were defined. The greatest unsolved problems were those of exact equipment size for several steps in the process and choice of materials of construction for some of the steps where highly corrosive solutions were present.

Major portions of the experimental work were devoted to the opening of the ore, the preparation of the extractor feed solution, and the separation of the niobium and tantalum by solvent extraction. Dissolution of the ore concentrate in aqueous 70 per cent hydrofluoric acid was determined to be the best method tested. This method was chosen in lieu of other methods because of the simplicity of operation.

Essentially 100 per cent opening of the ore was achieved when stoichiometric hydrofluoric acid and columbite ore were reacted for four hours at 100° C. Since the unit cost of hydrofluoric acid and columbite ore

together comprised more than 60 per cent of the final cost, this step was determined to be the most important part of the process. Any decrease in yield would have a strong influence upon the final manufacturing cost.

In the cost analysis the cheaper 66 per cent hydrofluoric acid was proposed for use over the more expensive 70 per cent variety. This somewhat weaker acid was not tested in the process and it is doubtful if any significant difference would be noted. Any future work on this process should include testing the effectiveness of the 66 per cent hydrofluoric acid on the opening of the ore concentrate.

Sulfuric acid dissolution of columbite ore was only moderately successful. Reaction with an acid to ore weight ratio of five to one resulted in approximately 70 per cent opening of the ore. However, the difficult filtrations necessary dictated that this method be dropped in favor of the hydrofluoric acid method. More research on the sulfuric acid method might result in a suitable process. The difference in raw material cost for the two acids definitely favor sulfuric acid. The extra processing steps which would be necessary if sulfuric acid were used could possibly reduce the advantages of the cheaper raw material be increasing the operating costs.

The best method for recovering the niobium and tantalum values from the hydrofluoric acid reaction mass was by leaching with hexone. Yields of 95-96 per cent were obtained when the reaction mass was leached countercurrently in four stages. The fourth leach was fresh hexone acidified to one normal with hydrofluoric acid. The use of acidified

hexone over fresh hexone increased the recovery of niobium and tantalum 2-3 per cent. The leach solution from the first contact with the reaction mass was used as the extractor feed solution.

In order to effect these high recoveries on a commercial scale, it was recommended that a filter such as the Bird Prayon or Eimco Pan be used. These filters are capable of high cake washing efficiency and sharp separation of filtrates, two features which are necessary to obtain high recoveries.

The wet fluoride cake discharged from the filter after the fourth leach contained 0.18-0.20 pounds of hexone per pound of solids. It was recommended that this hexone be recovered by simply drying in a vacuum-type shelf drier. Because of the possibility that some hydrofluoric acid remained in the cake, such a drier would have to be of a suitable material of construction such as monel clad steel.

The simulated column technique was used to predict the conditions for the continuous separation of tantalum and niobium by solvent extraction. Both diethyl ketone and hexone were employed as solvents for the separation. Diethyl ketone was a better extracting agent than hexone but the lower cost and higher recovery value of hexone dictated its use.

A continuous, nine-stage, mixer-settler extractor was used to demonstrate the relative ease with which tantalum and niobium can be separated. Tantalum with less than 100 ppm niobium, expressed as oxides, was produced in the extract product while the raffinate contained niobium with less

than 700 ppm tantalum. In both cases the purity values reported were the limit of the spectrographic methods employed. A second extraction, employing 15 stages, successfully extracted niobium into another hexone phase away from the impurities iron and manganese. Spectrographic analyses of the above extract products showed less than 50 ppm iron or manganese present.

The conditions employed for the above extractions were not necessarily the optimum. Since the best operating conditions are a function of a particular extractor and the feed solution composition, it was recommended that a pilot plant study be made on the extraction portion of the process before any scale up is attempted.

The best method for removing the solutes from the hexone extracts was found to be by direct precipitation with ammonium hydroxide. Several aqueous stripping solutions were tried, notably use of sulfuric acid, but none gave satisfactory results. The method settled upon was probably the least expensive operational wise since the hydroxide cakes had to be filtered under any conditions. The one disadvantage of the method was the eight per cent loss of hexone.

Solvent regeneration was accomplished by acidifying the hexone recovered from the hydroxide filtration step. The regenerated hexone was found to have increased extracting ability. This was probably caused by a small amount of hydrofluoric acid present in the hexone which resulted from the reaction of ammonium bifluoride and sulfuric acid.

One possible complication not investigated was the effect of solvent degradation. Regenerated hexone was dark brown in color as compared to clear virgin hexone. The dark color probably resulted from the presence of degradation products caused by the reaction of sulfuric acid and hydrofluoric acid with hexone. It is possible that the ten per cent replacement necessary to offset losses would control the degradation products and keep them at a permissible level. However, if this proved not to be the case, simple displacement of the solvent after a certain number of cycles could be used.

The plant chosen for the cost analysis was based upon 1000 pounds per day of separated oxides assaying 90 per cent niobium oxide and 10 per cent tantalum oxide. This size was roughly that of new zirconium purification facilities. It was considered that niobium would have to compete with zirconium for many of its proposed uses and hence this comparison was made to study the relative economic importance of niobium. Since the demand for tantalum-free niobium cannot be evaluated at this time, this size may be either too small or too large to fill projected niobium requirements. Change of estimated plant size would have greatest effect upon labor costs with some change in depreciation charges. It may be noted that these items comprised only a small fraction of the total manufacturing cost.

When possible, the choice of equipment for the projected plant was based upon requirements determined experimentally. In several instances equipment cost was estimated from general operating needs rather than

specific data. In particular, the size of storage tanks was based upon estimated requirements for inventory of raw materials and streams in process.

Most of the equipment proposed for the plant was constructed of haveg. The low initial cost of this material of construction over the noble metals was considered advantageous even though more care is necessary to properly maintain haveg. In most cases the utilization of haveg reduced equipment cost twenty-fold indicating that even a high rate of replacement could be tolerated.

Since most of the bulk manufacturing cost was derived from the raw material cost, notably the hydrofluoric acid, it was recommended that future research on this process be aimed at hydrofluoric acid recovery. Some reduction in raw material cost could be made by substituting sulfuric acid for hydrofluoric acid in the opening of the ore. However, as mentioned earlier, operating costs in this case might be raised to the point where no advantage is gained.

For the proposed process, there are two sources of hydrofluoric acid which might prove economical to recover. First, there is the fluoride cake consisting principally of iron and manganese fluorides. Secondly, the extracted niobium and tantalum solutions contain fluoride. In both cases sulfuric acid could be used to regenerate hydrofluoric acid. However, it is doubtful that either of these fluoride sources would prove economical for the production rate presently proposed.

From the cost analysis it was seen that either niobium or tantalum oxide could be produced for $2.80 per pound. Since the cost of the metal reduction for either metal was unknown, no final metal cost was estimated. On the other hand, high-purity niobium oxide presently costs around eighty-six dollars a pound. From a comparison of the above costs, it was evident that this proposed process could successfully compete with the processes presently employed.

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APPENDICES

APPENDIX A

Analytical Methods

Oxide concentration

Oxide concentration in aqueous solution. A volume of solution, containing approximately 500 milligrams of oxide, was diluted tenfold. Ammonium hydroxide was added to precipitate the niobium-tantalum hydroxide. A small volume of acetone was added to facilitate filtering. The niobium-tantalum hydroxide was filtered and dried. The hydroxide was ignited at 800° C. for two hours and weighed. The result was the weight of niobium-tantalum pentoxide.

Oxide concentration in organic solution. A volume of solvent, containing approximately 500 milligrams of oxide, was diluted tenfold with acetone. One to one ammonium hydroxide was slowly added to precipitate the niobium-tantalum hydroxide. The hydroxide was filtered, dried, and ignited at 800° C. The weight of solids was the weight of the niobium-tantalum pentoxide.

Tantalum-niobium ratio

The pentoxides were submitted to the spectrographic laboratory for the determination of the relative tantalum and niobium content by x-ray fluorescence (43) and spectrographic analysis (44). The first method was employed for mixtures containing between 2.0 and 98 per cent niobium and

was accurate to within ± 5 per cent. The spectrographic methods of Fassel and Krotz (44) were used for samples containing less than 2.0 or more than 98 per cent niobium. The accuracy of the spectrographic methods in these high purity ranges was ± 10 per cent of the minor constituent. The limit of detection for niobium in pure tantalum pentoxide was 50 parts per million while the limit for tantalum in pure niobium pentoxide was 700 parts per million.

Hydrofluoric acid concentration

The hydrofluoric acid concentration was computed from the total oxide concentration, the Ta/Nb x 100 ratio, and a total fluoride analysis. For the total fluoride analysis, the filtrate and all the washings from the total oxide determination were diluted to 100 milliliters in a volumetric flask. Ten milliliter aliquots of this solution was diluted approximately threefold with distilled water. If the solution being analyzed were organic, all dilutions and washings were made with ethyl alcohol. One milliliter of chloroacetic acid buffer solution (9.8 grams chloroacetic acid and 2.0 grams sodium hydroxide per 100 milliliters of water) was added and the pH adjusted to 3.0 with dilute hydrochloric acid. A pH meter was used in all cases. Several drops of alizarin red S indicator were added and the solution titrated with standard thorium nitrate solution until a permanent pink color resulted.

The moles of fluoride associated with H_2TaF_7 and H_2NbOF_5 were calculated from the total oxide concentration and the Ta/Nb x 100 ratio. The excess hydrofluoric acid normality was equal to the total moles of

fluoride minus the moles of fluoride associated with the H_2TaF_7 and H_2NbOF_5. These results were reproducible to approximately $\pm$ 3 per cent.

Minor elements

Calcined pentoxides were submitted to the spectrographic laboratory for analysis of the minor elements by emission spectrograph.

APPENDIX B

Table 22. Equilibrium data for pure niobium and tantalum fluorides with hexone

Volume of feed (ml)	Volume of hexone (ml)	Conc. of feed (moles oxides/liter)	Aqueous conc. (moles oxides/liter)	Organic conc. (moles oxides/liter)
H_2TaF_7 with 9.56 N excess hydrofluoric acid				
100	100	1.35	0.610	0.721
100	100	1.18	0.506	0.619
100	100	1.01	0.406	0.534
100	100	0.808	0.302	0.436
100	100	0.673	0.244	0.373
100	100	0.337	0.108	0.193
100	100	0.135	0.050	0.072
H_2TaF_7 with 1.60 N excess hydrofluoric acid				
100	100	2.24	1.56	1.10
100	100	1.96	1.30	0.925
100	100	1.68	1.10	0.770
100	100	1.40	0.866	0.637
100	100	1.12	0.669	0.515
100	100	0.839	0.460	0.398
100	100	0.560	0.286	0.276

Table 22. (Continued)

Volume of feed (ml)	Volume of hexone (ml)	Conc. of feed (moles oxides/liter)	Aqueous conc.(moles oxides/liter)	Organic conc.(moles oxides/liter)
100	100	0.280	0.143	0.132
100	100	0.134	0.074	0.062
100	100	0.090	0.045	0.035
100	100	0.045	0.028	0.013
$HTaF_6$ with 0 N excess hydrofluoric acid				
100	100	2.66	2.24	1.17
100	100	2.44	1.94	0.982
100	100	2.22	1.85	0.909
100	100	2.00	1.60	0.804
100	100	1.77	1.42	0.690
100	100	1.54	1.17	0.587
100	100	1.33	0.984	0.501
100	100	1.10	0.786	0.415
100	100	0.878	0.600	0.331
100	100	0.666	0.436	0.254
100	100	0.399	0.255	0.154
100	100	0.226	0.151	0.082
100	100	0.160	0.109	0.053
100	100	0.106	0.075	0.031
100	100	0.053	0.035	0.013

Table 22. (Continued)

Volume of feed (ml)	Volume of hexone (ml)	Conc. of feed (moles oxides/liter)	Aqueous conc.(moles oxides/liter)	Organic conc.(moles oxides/liter)
H_2NbOF_5 with 13.52 N excess hydrofluoric acid				
100	100	2.25	2.22	1.13
100	100	1.97	1.95	0.832
100	100	1.69	1.66	0.722
100	100	1.41	1.40	0.521
100	100	1.13	1.10	0.341
100	100	0.732	0.845	0.184
100	100	0.563	0.202	0.064
H_2NbOF_5 with 6.0 N excess hydrofluoric acid				
100	100	3.21	2.92	1.06
100	100	2.81	2.47	0.895
100	100	2.41	2.18	0.722
100	100	2.00	1.77	0.519
100	100	1.60	1.48	0.344
100	100	1.04	1.14	0.186
100	100	0.802	0.781	0.059